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"MODELING AND EXPERIMENTAL STUDIES OF OXIDE COVERED METAL SURFACES: TiO_2/Ti A MODEL SYSTEM"

A Progress Report and Continuation Request

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I. SUMMARY AND HIGHLIGHTS OF PROGRESS

Prior work in our laboratories at the Corrosion Research Center has shown that thin, anodic TiO_2 films formed by the Slow Growth Mode (SGM) on polycrystalline titanium are microcrystalline with a texture that varies from one metal grain to another. Furthermore, the underlying metal grains are mapped by the photoelectrochemical response of the oxide. The same characteristics have also been demonstrated in our laboratory for ZnO grown on Zn. The TiO_2/Ti system has been chosen for study both because of its importance in energy systems, and because it can serve as a model system for other metal-metal oxide couples. It is known that the crystallographic orientation of the substrate has been found to influence the dissolution current density, and the current in the passive range on titanium (Ruff and Fraker, 1974). The difference in current in the passive range probably reflects the relative defect concentration in the oxide grown on different grain orientations. Therefore, knowledge of the local defect concentration in the oxide provides a basis for predicting relative corrosion rates in the passive region. Such a correlation may also describe the pitting corrosion susceptibility of different metal orientations as well.

The investigations of anodic TiO_2 films on Ti have shown that the properties of thin films are consistent with the rutile form of the oxide. Both experimental data and theoretical calculations show the close resemblance to results on single crystal TiO_2 (Koffeyberg, et al. 1979). Furthermore, the modeling studies reveal that the optical transitions near the bandedge arise from the bulk band structure.

The photoelectrochemical properties of anodic TiO_2 films have now been shown to obey the simple Gaertner-Butler model for the semiconductor-electrolyte interface, with a few modifications. The most important deviation has now been shown to be a result of multiple internal reflections in the oxide film. This causes the photocurrent at 351 nm wavelength to increase with film thickness (up to about 30 nm) due to constructive interference. Without the multiple reflection effect, the photocurrent would be expected to be constant for films thicker than the depletion layer thickness (approximately 5 nm for our films). Further, the film behavior is dominated by the oxide/electrolyte interface. The surface charge density (mapped by Kelvin Probe Microscopy), surface sensitive photoelectrochemical microscopy (s-PEM), and other measurements point to surface recombination as the controlling factor which determines photocurrent contrast from grain to grain. This is to be contrasted with the behavior of Al/Al_2O_3 and Hf/HfO_2 where internal photoemission at the metal/metal oxide interface controls the behavior. We have obtained in situ internal photoemission maps of Al/Al_2O_3 surfaces for the first time.

Surface sensitivity of x-rays has been demonstrated for grazing incidence conditions. The first-ever x-ray scattering and reflectivity results for anodic oxide films have been obtained by our group. The x-ray scattering measurements were carried out on slow growth mode TiO_2 on Ti single crystals in the $(11\bar{2}0)$, (0001), and $(10\bar{1}0)$ orientations. It was found that **the oxide phase was controlled by the substrate orientation** for thick films (~27 nm). The first-ever in situ x-ray scattering measurements were carried out on the same films. In situ and ex situ (helium) results agreed with one another very well. X-ray reflectivity measurements were carried out on Ta_2O_5 and Nb_2O_5 anodic films and the results will appear in an Electrochemical Society Symposium Proceedings volume as well as Surface Science. The film thickness and interfacial roughness was measured for the anodic films as a function of formation voltage. The film thickness increased linearly with voltage for each oxide film.

Scanning tunneling microscopy (STM) and tunneling microscopy (TS) studies of anodic TiO_2 films have shown that the density of electronic states and bandgap depend on the film thickness. The native TiO_2 film shows a very high surface density of states (SDOS) and increased electronic state density at energies corresponding to the bandgap region. The STM has also been used to induce pits on TiO_2 films. The first-ever SDOS measurements show agreement with theoretical calculations.

II. THEORTICAL AND PHOTOELECTROCHEMICAL INVESTIGATIONS OF ANODIC OXIDE FILMS

IIA. ELECTRONIC STRUCTURE OF ANODIC TiO_2 LAYERS

J.W. Halley

Research Associates: Marek Michalewicz, Xiao Fang Wang

Graduate Student: Nacir Tit

1. RESULTS

The theoretical work in Professor Halley was group was focussed on two distinct problems associated with corrosion science. As a part of the Corrosion Center effort to understand the passivation layer, we are carrying out calculations of the electronic structure of TiO_2 disordered by oxygen vacancies. Research associates Marek Michalewicz and Xiao Fang Wang and graduate student Nacir Tit are involved in this effort which is closely coupled to experimental work by the groups of W. Smyrl and H. White of the Corrosion Center.

Our work on a detailed model of the TiO_{2-x} passivation layer disordered by oxygen vacancies, based on innovative numerical methods developed earlier (Halley and Shore, 1987), was published in Physical Review B (Halley et al., 1990). The results were compared with experiments by Professor Smyrl and M. Kozlowski on the photoconductivity of the passivation layer in a paper accepted for publication in Surface Science (Halley et al., in press). The main conclusion of this lengthy paper comparing theory and experiment is that band gap states do not appear in the observed photoconductivity data and the observations can be understood entirely in terms of the bulk band structure of bulk TiO_2. We suggested that this is because the band gap states are localized. To explore this possibility we continued work on the d.c. and optical conductivity of the models of TiO_2 as described in the next paragraph. A preliminary comparison of our model with Scanning Tunneling Microscope results of H. White and coworkers at the Corrosion Center on the density of states of TiO_{2-x} films was presented

(Tit et al., 1991) at the 13th Symposium on Applied Surface Analysis in June 1991. The theoretical results are remarkably similar to the experimental ones, though more work on the parameterization of the defect potential is required to clarify the quantitative meaning of the comparison. New studies of the fluctuation of energy levels using our methods were reported at the American Physical Society March meeting (Shore, et al., 1991). We compare our results with predictions by Altschuler and Shklovski (1986) on the expected behavior of the fluctuations at the metal insulator transition. The results are partly consistent with the theoretical speculations of Altschuler and Shklovski (1986) but details are somewhat unexpected. Interpretation of these results on fluctuations will be carried out in collaboration with Professor Shklovski, who holds a chair in the new Theoretical Physics Institute at the University of Minnesota. For the study of single defects, we carried out a comparison of our methods with traditional green function methods (Tit and Halley, 1991). The somewhat unexpected conclusion is that in cases in which the defect potential is of finite range, our equation of motion methods are numerically superior. A longer paper is in preparation on the work on green function methods.

Our work with H. Shore on the frequency dependence of the very low frequency conductivity of strongly disordered metals was published in Physical Review Letters (Shore and Halley, 1991). (The work was also reported in a talk at the Localization 90 conference in London in August 1990). In this paper, we reported new numerical methods which permitted us to calculate the low frequency dependence for the well known Anderson model of a disordered conductor for the first time and to compare the results with various approximate analytical calculations reported earlier. A second method (Halley et al., in press) for calculating the conductivity was extensively tested on the simplified model for TiO_2 reported in Halley and Shore (1987). The new results show for the first time how an impurity band arises from oxygen vacancies in the model. We have calculated the function $\sigma(E)$ which gives the d.c. conductivity of the sample if E is the Fermi energy. We find that the band gap states, which are localized and do not contribute to the conductivity at low oxygen vacancy concentrations, lead to a conducting band only when there are at about 9% oxygen vacancies in this model and are localized at lower vacancy concentrations. The possibility of such effects, giving an impurity band as a consequence of a kind of quantum percolation between defects, have been discussed many times but have never been shown to occur in a detailed model before to our knowledge. The result is qualitatively consistent with the idea, which we proposed in Halley et al., (in press) that the reason that no band gap states were observed in the photoconductivity experiments by Kozlowski and Smyrl is that the band gap states are localized in those samples.

Work on the inclusion of coulomb interactions in the code continued. The Hartree code described in earlier proposals has not yet achieved numerical self-consistency, but preliminary results are sufficiently promising to warrant continued work on this program as personnel and resources allow.

IIb. SURFACE SENSITIVE PHOTOELECTROCHEMICAL MICROSCOPY (s-PEM)

W.H. Smyrl

Research Associate: C.S. McMillan

1. RESULTS

The effect of the local nature of semiconducting oxide films on their performance as electronic materials, corrosion inhibitors, and in fields such as solar energy conversion warrant thorough investigative efforts. To this end several studies relating structural and photoelectrochemical properties of anodically grown, thin (<20 nm) TiO_2 films to their polycrystalline Ti substrates have been undertaken (Kozlowski et al., 1989; Tyler et al., 1987; Kozlowski et al., 1988; Paik, et al., 1988). Photoelectrochemical microscopy (PEM), in which a focused laser beam is used to generate localized photocurrents, has revealed the important influence of the substrate grain orientation and oxide characteristics on the optical and electronic properties of the films. PEM studies have shown the photoelectrochemical properties of such thin TiO_2 films on polycrystalline Ti substrates to be heterogeneous and dependent on oxide growth rate and substrate crystallography (Kozlowski et al., 1989). We report here an extension of the PEM technique which appears to be sensitive to the density of positively charged surface species.

The method is based on the derivatization of TiO_2 with ferrocyanide as reported by Vrachnou, Gratzel and McEvoy, (1989) which extends the photoresponse of TiO_2 into visible wavelengths. Use of visible wavelength light (i.e., energy less than the TiO_2 bandgap) to generate a PEM image of treated TiO_2 brings about a considerable surface sensitivity. The photoresponse of the oxide interior which relies on band-to-band absorption is shut off, and the local photocurrent depends instead on the density of surface/ferrocyanide complexes. Such complexes are assumed to form where positively charged species are present at the surface, for example oxygen vacancies or titanium interstitials.

The photocurrent is generated by promoting an electron from the surface-situated complex to the TiO_2 conduction band. The oxidized complex is then reduced by hydroquinone and/or ferrocyanide in solution. Because virtually all electron promotion takes place at the oxide surface, only a small anodic bias is required to drive electrons into the interior. Increasing the bias does not increase the photocurrent, indicating the insignificance of electron-hole pair generation in the oxide interior.

In combination with PEM images made using above-bandgap illumination, subbandgap PEM of treated TiO_2 surfaces allows one to compare and contrast surface and interior or 'bulk' oxide behavior.

Subbandgap PEM images of the ferrocyanide treated TiO_2 surfaces tend to show show grain to grain maps nearly identical to PEM images produced by above bandgap illumination. The similarity of the images indicates the controlling nature of the surface in the production of photocurrent. High densities of surface states are believed to be the primary reason for the strong surface influence.

In summary, subbandgap PEM of ferrocyanide-treated TiO_2 can be used to map the density of positively-charged surface species on anodically grown TiO_2. Potentially, areas susceptible to chemical or electrochemical attack can be indicated nondestructively with this technique. In combination with above-bandgap PEM it enables the comparison of surface and bulk photoelectrochemical properties arising form variations in substrate preparation, oxide growth parameters, and oxide modifications.

This work was presented at the Seattle meeting of the ECS (October 1990). It will appear in Applications of Surface Analytical Techniques to Metal-Environmental Interactions, Eds. G. Davis, et al., Electrochemical Society, Pennington, NJ, 1991.

IIc. MULTIPLE INTERNAL REFLECTION EFFECTS IN THIN OXIDE FILMS

W.H. Smyrl

Graduate Student: J.H. Sukamto

1. *RESULTS*

The following discussion applies to thin films in general, and thin absorbing films in particular. An anomaly associated with thin films is the interaction between internally reflected beams, which must be summed coherently. In addition to increased absorption, coherent summation of multiple internal reflections leads to optical interference effects. Furthermore, we have found that, combined with a simplified Gartner/Butler expression, the dependence of the quantum efficiency on film thickness can be explained in terms of multiple internal reflections (Sukamto, et al., 1990).

The classical treatment of multiple internal reflections can be found in many excellent references; one of the most comprehensive is that by Knittl (1976). That multiple internal reflections affect photoelectrochemical measurements on thin films is recognized, see for example Peter, 1987; Popkirov and Schindler, 1986; Popkirov and Schindler, 1987. However, the treatments given so far are somewhat limited. In Peter (1987), discussions were limited to 2 passes within the film, and only the total absorption was given, which obscured the role of multiple reflections in determining surface parameters such as the surface recombination velocity (further discussions below). In Popkirov and Schindler (1986) and Popkirov and Schindler (1987), discussions were limited not only to 2 passes, but also to incoherent summation of the beams within the absorbing thin film.

We have examined the differential absorption within a thin film, computed directly from coherent summation of the inner field. The specific system to be presented is a three-layer model, in which the thin absorbing, homogeneous TiO_2 film is sandwiched between a thick non-absorbing, homogeneous electrolyte medium and thick, absorbing, homogeneous metal substrate. General relations applicable to all materials satisfying the restrictions mentioned above were used. In order to make numerical comparisons we restrict discussions to thin, anodically grown TiO_2 on Ti immersed in H_2SO_4. Comparison of results for a single pass and a number of passes (including an infinite number of passes) have shown that varying the film thickness shifts the location where the maximum differential absorption occurs; it does not necessarily occur at the illuminated surface. Consequently, values for the surface recombination velocity derived from photoelectrochemical measurements will change depending on the number of internal reflections considered. Another effect of multiple internal reflection is the amount of light absorbed by the film; here, again, varying the film thickness leads to interference effects within the film which change the integral of the differential absorption (or the total absorption). We note that the photocurrent on thin TiO_2 films on Ti increases with thickness in the range 5 - 17.5 nm. By correlating the calculations to the measured photocurrent at one voltage and film thickness, the data at other thicknesses are modeled successfully, see e.g., Fig. 1.

A preliminary version of this paper was presented at the Seattle Meeting of the Electrochemica Society, October 1990, and will appear in Applications of Surface Analytical Techniques to Metal-Environmental Interactions, Eds. G. Davis, et al., Electrochemical Society, Pennington, NJ, 1991. A fully developed paper was presented at the Washington Meeting of the Electrochemical Society, May 1991, and the paper has been submitted to the Journal of the Electrochemical Society.

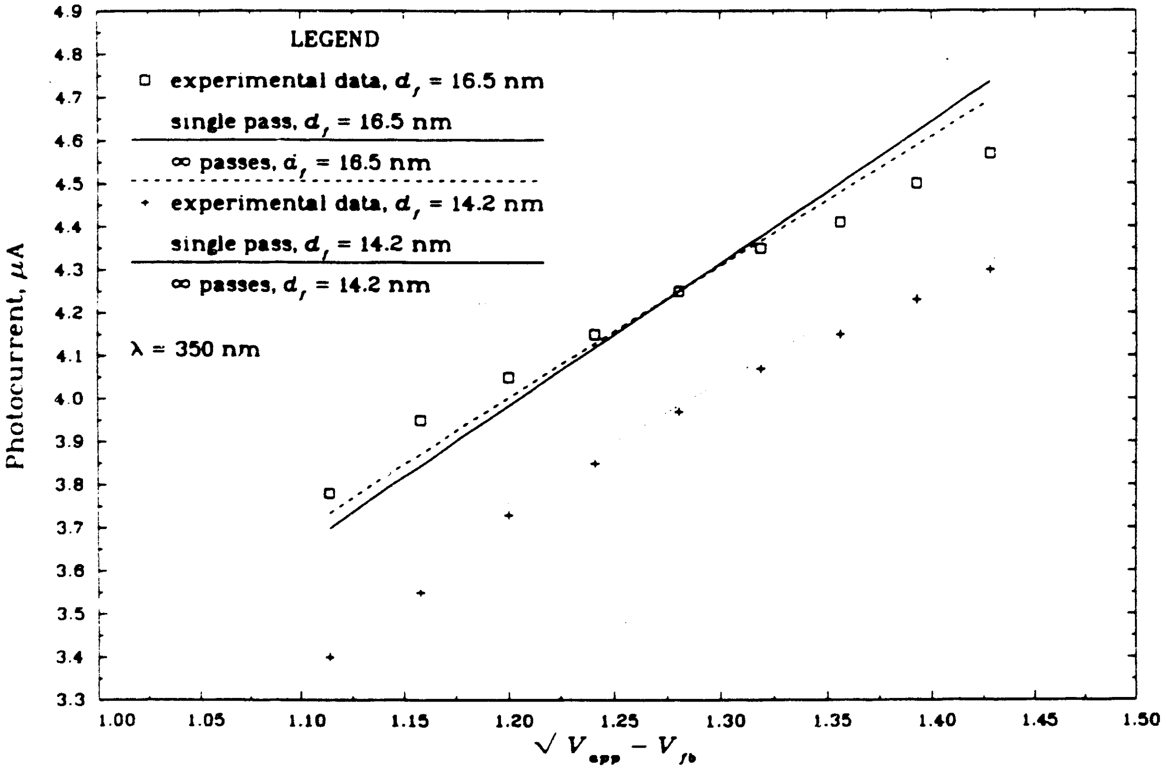

Figure 1. Comparison of the experimental and theoretical photocurent as a function of applied bias at two films thicknesses. The solid line is the theoretical photocurrent for a single pass using the Gaertner-Butler model. The dotted lines are the theoretical photocurrents for infinite passes using the Gaertner-Butler model.

IId. INTERNAL PHOTOEMISSION STUDIES OF Al/Al_2O_3 AND Hf/HfO_2 SYSTEMS

W.H. Smyrl

Research Associate: C.S. McMillan

1. *RESULTS*

The importance of Al_2O_3 in a wide variety of applications (ex. corrosion protection, capacitors, electronic device substrates) warrant an examination its electronic properties. Photoelectrochemical study provides in-situ information on the spatial inhomogeneities in the oxide films as well as on electronic variation of a given area. The films were formed by galvanostatic oxidation of aluminum in a solution of ammonium pentaborate in ethylene glycol. Films formed in this way are reported to include no free solvent and growth is almost 100 percent efficient (Bernard and Cook, 1959). Two photoelectrochemical methods were employed; photocurrent spectroscopy, in which the photocurrent is measured as a function of excitation wavelength to provide a measure of the optical gap energy, and photoelectrochemical microscopy (PEM) in which a focussed laser beam is rastered across the oxide to provide resolution of spatial inhomogeneities. Photocurrent spectroscopy has revealed both anodic and cathodic photocurrents. Fowler plots showing a linear dependence of the square root of the cathodic photocurrent on the photon energy indicate that internal photoelectron emission originating at the metal/metal-oxide interface dominates the photocurrent generation. Internal photoemission is illustrated in Figures 1a and 1b. The photocurrent spectrum is strongly affected by the oxide growth conditions. The potential dependence of the photocurrent response is qualitatively similar to that seen for anodic HfO_2 (see below) suggesting similar generation mechanisms. Photoelectrochemical microscopy (PEM) at cathodic and anodic potentials has produced internal photoemission maps. Figure 2a and 2b show cathodic and anodic photocurrent images, respectively. Internal photoelectron emission in plasma grown Al_2O_3 has also been reported by Goodman (1970) and internal photohole emission has been observed by

Di Quarto (1991) for anodic aluminum oxide films. The dominance of the metal/metal oxide interface on these amorphous Al_2O_3 films on Al stands in contrast to the dominance of the metal-oxide/solution interface seen in the case of crystalline anodic TiO_2 on Ti.

Interest in the electronic nature of HfO_2 has arisen in the field of laser mirror coatings recently, and in a more general sense stems also from its membership in a group of wide bandgap oxide semiconductors. This study focusses on the photocurrent spectroscopy of anodically grown thin films of HfO_2 on single crystal Hf as part of an ongoing series on the photoelectrochemical nature of metal oxide films. Anodically grown HfO_2 produces both an anodic and cathodic photocurrent. As with anodic barrier type aluminum oxide, the sign of the photocurrent changes direction as a function of the wavelength at low applied potentials. At strongly anodic or cathodic potentials, internal photohole emission and internal photoelectron emission strongly influence photocurrent generation. The results show the preeminence of the metal/metal-oxide interface in controlling the photoresponse.

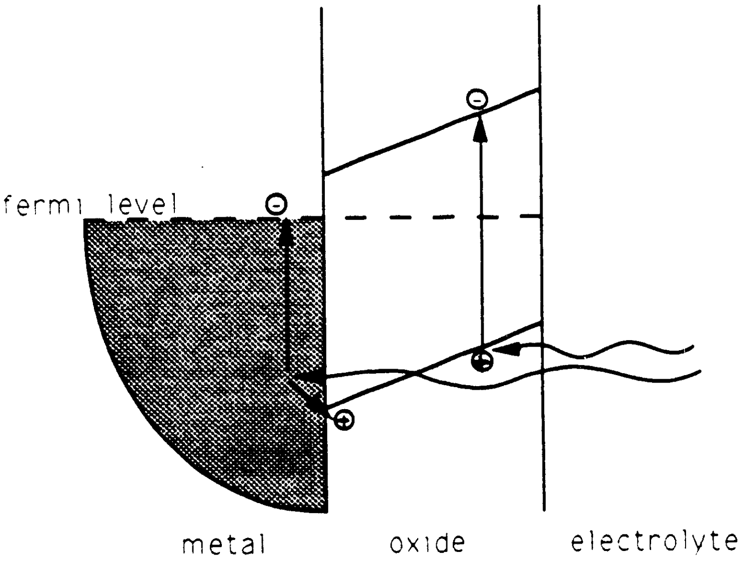

Figure 1a. Internal photohole emission involves the injection into the metal-oxide valence band of a photoproduced hole from the metal. Under anodic bias this process can produce a photocurrent along with valence band to conduction band excitation which is also shown.

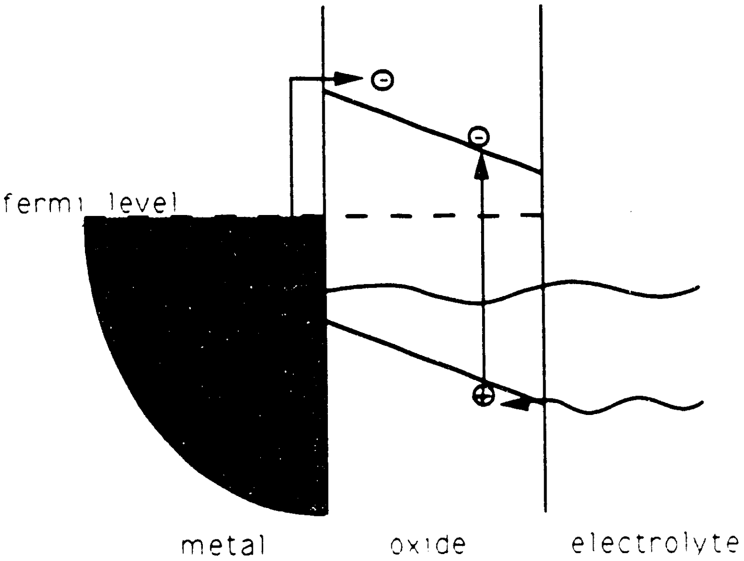

Figure 1b. Internal photoelectron emission involves the injection into the metal-oxide valence band of a photoproduced electron from the metal. Under cathodic bias this process can produce a photocurrent along with valence band to conduction band excitation which is also shown.

Figure 2a. Photoelectrochemical micrograph (PEM) of anodic aluminum oxide under cathodic bias.

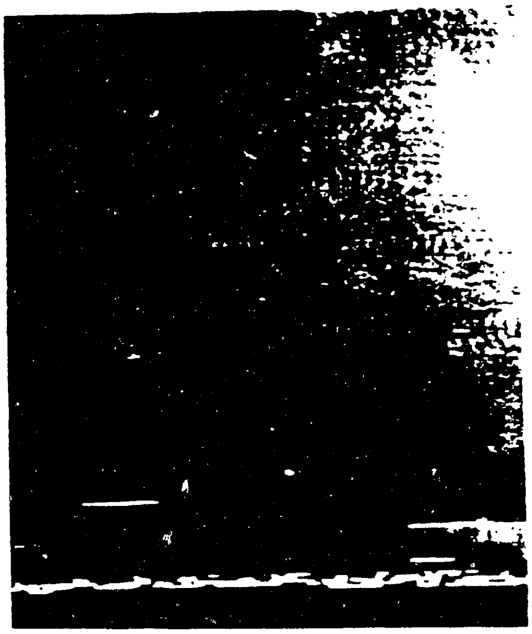

Figure 2b. PEM of the same region of anodic aluminum oxide under anodic bias.

III. SURFACE X-RAY STUDIES OF THIN OXIDE FILMS

M.F. Toney, Owen R. Melroy, William H. Smyrl

Research Associates: David Wiesler and C.S. McMillan

IIIa. STRUCTURE AND EPITAXY OF THIN ANODIC TiO_2 FILMS ON LOW-INDEX TITANIUM SURFACES

1. RESULTS

The breakdown and corrosion of passive oxide films are often associated with mechanical processes, such as film rupture, loss of adhesion, and stress-related phenomena. Understanding these causes requires a detailed knowledge of the atomic structure, phase composition, and strain of the passive film, as well as its orientation with respect to the metal substrate (i.e., its epitaxy). Despite extensive study of anodic films, their structure and epitaxy are in general poorly understood (Frankenthal and Kruger, 1978).

Structural information comes from two sources. Indirect methods, such as Raman scattering, capacitance measurements, or bulk stress measurements, *infer* structural properties of the film from comparison of experimental data with the known properties of bulk oxides. Direct structural measurements are less common. These typically use electron diffraction (RHEED or LEED) to measure atomic positions within the film and the metal substrate. Electron diffraction, however, is limited by the inability of electrons to penetrate macroscopic aqueous layers, making in situ measurements impossible. A second problem is the possibility of inducing crystallization by the electron beam (Leach and Pearson, 1988). Finally, structure determinations from electron diffraction require complicated dynamical models. All three limitations can be overcome by surface x-ray diffraction, as demonstrated in recent in situ studies of electrochemical interfaces (Samant et al., 1988; Toney et al., 1990; Ocko et al., 1990). We present here the results of x-ray diffraction studies of anodic oxides on low-index crystal surfaces of titanium.

The titanium samples used in these experiments were cut from single crystal rod and oriented to within 2° of $(11\bar{2}0)$ and $(10\bar{1}0)$. Crystals were mechanically polished, electropolished, and chemically etched in an aqueous solution of 2% IIF and 4% HNO_3 to remove residual oxide left from electropolishing. Anodic oxides were grown at 0.1 mV/sec from open circuit in 0.1 N H_2SO_4 to 6-10 V (vs. SCE), where they were held for several hours. The slow growth is thought to favor more crystalline oxides, closer in structure to native films (Kozlowski, 1989). Oxides were 200-300 Å thick. The x-ray diffraction was performed using a Huber 4-circle diffractometer on the focused beam lines X-20A and X-20C of the National Synchrotron Light Source (NSLS).

On the $(11\bar{2}0)$ face of Ti, we have observed diffraction peaks for both the anatase and rutile forms of TiO_2, shown respectively as solid and dashed arcs in the reciprocal space diagram in Fig. 1. Rutile is found to be nearly epitaxial, with its *a* and *b* axes aligned on average with the in-plane Ti $(1\bar{1}00)$ and (0001) axes and its *c* axis normal to the film. Anatase exhibits a more complex orientation with respect to the Ti substrate. From the radial widths of the diffraction peaks, the rutile and anatase domain sizes are found to be quite small, ~40 and 80 Å, respectively.

Because of the greater orientational order of the rutile, it is plausible that rutile is in contact with the Ti surface. Figure 2 shows a real space schematic of the rutile/Ti $(11\bar{2}0)$ interface. The rutile *a*- and *b*-axes are on average in the Ti $(1\bar{1}00)$ and (0002) directions, which is intuitively reasonable, since in these directions the mismatches between the rutile and Ti lattices are only 10% and 2%, respectively. Since the growth of TiO_2 occurs predominantly at the metal-oxide interface (Khalil and Leach, 1986), Fig. 2 suggests a possible microscopic growth model for the incorporation of the O^{2-} anions into the Ti lattice. The Ti substrate atoms at the corners of the rectangular dashed cell (Fig. 2) remain essentially stationary, while the atom at the face-center of the dashed cell (marked by the *f*) moves to the center of the cell. The two other Ti atoms in the dashed cell (marked by the *o*) move up through the interface and are incorporated into the oxide. This model is highly speculative, but it reproduces the epitaxial arrangement we have observed and agrees with the measured transport numbers (Khalil and Leach, 1986).

The Ti $(10\bar{1}0)$ face exhibits an oxide structure that is similar to that for Ti $(11\bar{2}0)$ in several ways. Both rutile and anatase are observed, and they have essentially the same domain sizes as on the Ti $(11\bar{2}0)$ surface. The anatase similarly exhibits a uniaxial orientational preference, with disorder about this axis. An important difference between the two crystal faces is the absence of a well-ordered rutile structure on the Ti $(10\bar{1}0)$ surface. This is particularly surprising, since there exists an epitaxial configuration with very small lattice mismatches (<2% in each direction) for this face.

Finally, we have also carried out <u>in situ</u> x-ray scattering studies on the (0001) surface of Ti. The data for all three orientations is summarized in Table 1. The surprising finding that the films have a large fraction of anatase (nearly 100% on the (0001) surface) may be due to the film thickness. It has been noted in the literature that thin TiO_2 films are dominantly rutile, but thick films are anatase - consistent with the present results. Because of the roughness, we were unable to verify that rutile may be retained at the inner interface, with the anatase phase occupying the outer regions of the film. We hope to do such "depth profiling" in the future.

TABLE 1

	RUTILE	ANATASE
Ti$(11\bar{2}0)$	nearly epitaxial	textured powder
Ti $(10\bar{1}0)$	textured powder (small amount)	textured powder
Ti(0001)	not observed	textured powder
Domains:	40Å	80-100Å
Strain:	.08 ± .06% (expanded)	.24 ± .03% (expanded)

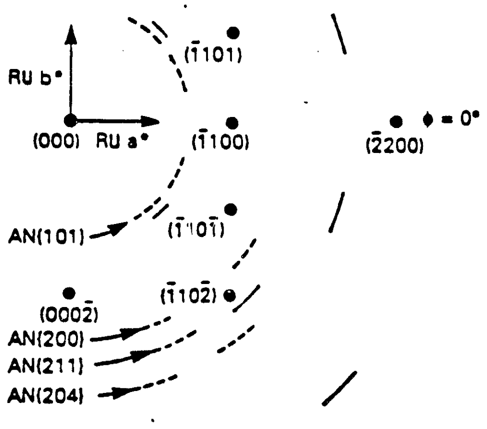

Figure 1. Diffraction pattern for anodically oxidized Ti(11$\bar{2}$0). The Ti in-plane reciprocal lattice is shown by solid points. The rutile and anatase diffraction peaks are indicated by solid and dashed arcs, respectively.

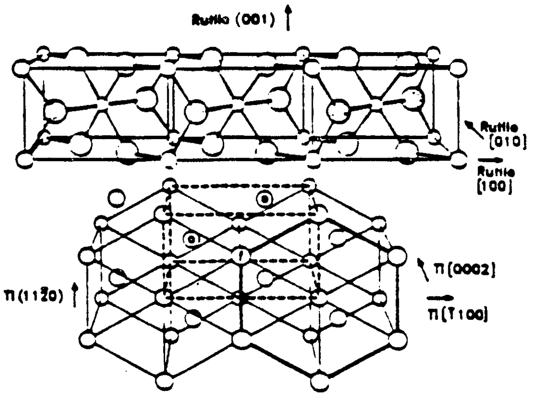

Figure 2. Real-space representation of the epitaxial relationship between rutile and Ti(11$\bar{2}$0). The open and filled spheres represent Ti and O atoms, respectively, and the thin lines in the rutile show the unit cells. The lines in the Ti connect atoms on one of the sublattices, whereas the atoms in the other sublattice are not connected. The heavy lines indicate one of the hexagons in the Ti basal plane. The dashed lines shown one of the rectangular cells that are easily transformed into rutile (see text).

IIIb. INTERFACIAL DENSITY PROFILE OF ANODIC OXIDES OF Ta AND Nb MEASURED BY X-RAY REFLECTIVITY

In an x-ray reflectivity experiment, x-rays impinge on a flat sample at a grazing angle, and the specularly reflected intensity is measured as a function of scattering angle 2θ. X-ray reflectivity is similar in form to optical reflectivity, but differs from it in two important regards. First, the index of refraction at x-ray wavelengths is slightly less than one, and as a consequence x-rays at sufficiently small angles are totally reflected. Second, since x-ray wavelengths are on the order of the thicknesses of adsorbed layers of thin films, interference between waves reflected at different interfaces is readily detected. This second property makes thickness measurements of passive oxide films highly accurate and relatively easy to perform. In addition, no *ad hoc* assumptions of optical constants, stoichiometry or microstructure. X-ray reflectivity furthermore can obtain interfacial widths or interdiffusion, in contrast to more conventional tools, which measure only the average layer thickness.

We report here x-ray reflectivity measurements on a series of anodic oxides of Ta and Nb. The metal films were grown by sputter deposition onto soda-lime glass slides to a metal thickness of 2000 Å. Anodization was carried out in 0.1 N H_2SO_4 by ramping the potential at 0.1 mV/sec from open circuit to the growth potential, measured against a standard calomel reference electrode. Following growth, the electrode was kept at the final potential several hours to allow the film to relax. X-ray measurements were carried out at the Center for Materials Research at Stanford University, using an 18 kW Rigaku rotating anode Cu Kα source (λ = 1.542 Å) and a pyrolytic graphite monochromator.

Figure 1 shows a representative x-ray reflectivity spectrum of a 5 V Ta_2O_5 film. The dashed and dotted lines are drawn for Ta and Ta_2O_5, respectively, and represent Fresnel curves, which describe the scattering that would obtain for a perfectly smooth Ta (or Ta_2O_5) film. The data are unlike the Fresnel curve in two respects. First, oscillations in the data arise from interference between reflections at the oxide/air and metal/oxide interfaces. The periodicity of these oscillations is inversely proportional to the mean oxide thickness. Second, the observed reflectivity falls more rapidly than the Fresnel curve due to interfacial and surface roughness. Detailed fits of the reflectivity curves were carried out for each film. Figure 2 shows a representative fit to a 6-volt anodic oxide of Ta.

The oxide thickness as a function of growth potential is shown in Figure 3 for Ta and Nb films. The oxide film growth is linear, in agreement with the literature, with a rate of 22.3 ± 2.0 Å/V, extrapolating to 21 ± 7Å at 0 V. The zero-potential thickness presumably is due to a native oxide. We have found that both interfaces become smoother with increasing growth potential for Ta, but for Nb there is no clear variation of the roughness and growth potential.

In conclusion, we have demonstrated that x-ray reflectivity can be used to yield oxide film profiles with good accuracy and depth resolution, without any assumptions of optical response, density, or stoichiometry. We find that for slowly grown oxides of Ta and Nb the growth is linear with potential, and that for Ta films the roughness appears to decrease for thicker films.

While the experiments described here were performed ex situ, x-ray reflectivity is readily adapted to in situ growth experiments, since x-rays can penetrate macroscopically thick aqueous layers.

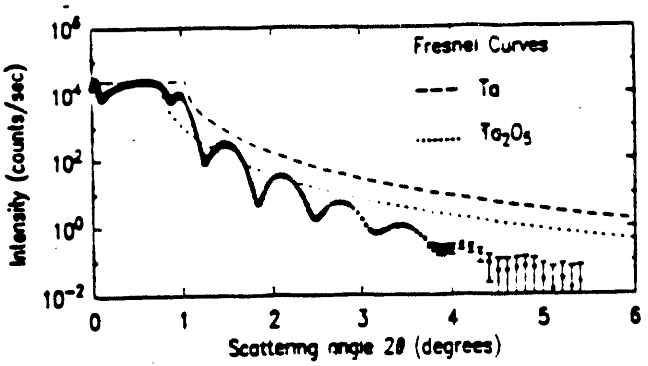

Figure 1. A representative x-ray reflectivity spectrum of a 5 V Ta_2O_5 film. Theoretical scattering curves for perfectly smooth Ta and Ta_2O_5 films are shown as the dashed and dotted lines, respectively.

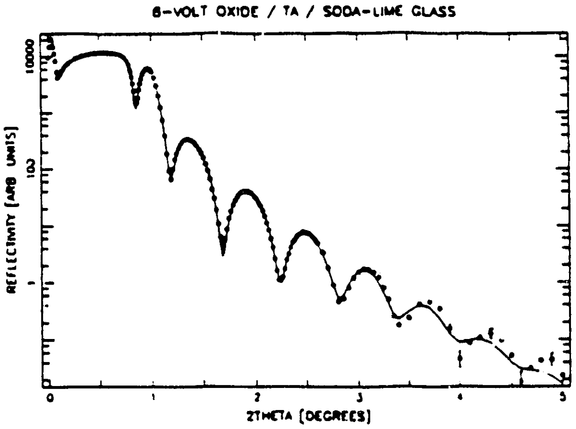

Figure 2. A representative fit to a 6 V anodic oxide of Ta.

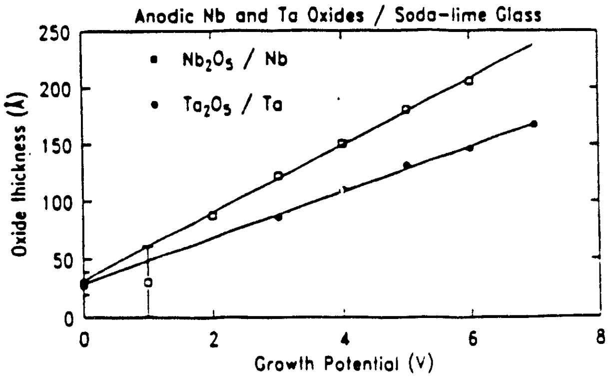

Figure 3. Variation of the oxide thickness for Ta and Nb anodic oxides with growth potential.

IV. SCANNING TUNNELING MICROSCOPY AND TUNNELING SPECTROSCOPY OF ANODICALLY GROWN TiO_2 FILMS

H. S. White and W. H. Smyrl

Graduate Students - Norberto Casillas and Christopher P. Smith

1. RESULTS

Our experimental studies have focused on the electronic properties of TiO_2 films and their relationship to electron-transfer and corrosion reactions. The primary experimental methods have been scanning tunneling microscopy and tunneling spectroscopy. Work has been completed or progressed significantly in the four major areas summarized below. Results from these investigations will be presented by Professor White in an invited presentation at the 1992 Gordon Conference on Electrochemistry.

A) *Density of Electronic States of TiO_2 Films.* We have completed (Casillas et al., 1991a) a detailed comparison of the surface density of states (SDOS) on native TiO_2 films, anodically grown TiO_2 films (160 Å), and the (001) and (110) surfaces of single crystal rutile TiO_2. SDOS plots for anodically grown TiO_2 films and single crystal TiO_2 show a large band-gap region (~2 eV) with a low state density separating the conduction band and valence band edges. The similarity in the distribution of SDOS for anodically grown TiO_2 thick films and single crystal TiO_2 strongly suggests that the anodically grown film has a well-ordered rutile structure. In contrast, SDOS plots obtained on native TiO_2 films show a nearly constant density of states over a 5 eV range and a ~20-50 fold increase in the electronic state density at energies corresponding to the band-gap region of anodically grown TiO_2, Figure 1. We speculate that the absence of a well define bandgap for native oxide films may be a consequence of tunneling across the thin native oxide, or a large defect density in the native TiO_2 film due to oxygen vacancies or interstitial Ti^{3+}.

The relatively large value of the SDOS observed for native oxide films suggests that the thin films may have large numbers of surface electronic states available for electron-transfer reactions involving redox species that have electrochemical potentials within the bandgap region of TiO_2. This hypothesis has important consequences in corrosion reactions that involve the oxidation of the substrate by a molecular oxidant, e.g., O_2. To test this hypothesis, we have measured and compared the voltammetric response of native and anodically grown TiO_2 films in acetonitrile solutions containing ferrocene (Casillas et al., 1991a). In these experiments, ferrocene was used as a model redox compound that is capable of transferring electrons to TiO_2 if the SDOS is sufficiently large. We observed that the rate at which ferrocene is oxidized in the electrochemical experiment correlates very well with the measured density of states obtained from tunneling spectroscopy, Figure 2. We believe that these latter measurements represent the first attempt to quantitatively correlate measurable heterogeneous electron-transfer rates with the surface electronic properties of oxide films.

B) *STM-Induced Pitting of Oxide Films.* In a preliminary account (Casillas et al., 1991b), we demonstrated that the electric field surrounding the tip of a STM could be used to induce breakdown of TiO_2 films. The goal of these experiments was to probe, in a controlled fashion, the mechanisms of pitting and corrosion cracking in oxide films. Figure 3 shows STM images of an individual pit (Fig. 3a) and crack (Fig. 3b) created on TiO_2 films by positioning the STM tip, without scanning, in close proximity of the surface (within a few angstroms). The voltage bias between the stationary tip and the TiO_2 substrate was linearly cycled (80 V/s) between predetermined positive and negative limits while the distance between the tip and surface remained constant. Repeated cycling of the voltage resulted in the removal of the TiO_2 layer in the region beneath the tip and the generated nanometer wide cracks extending from the surface region beneath the tip. The size of the pit can be controlled by adjusting the initial tip-to-substrate distance and/or the potential range scanned during removal of the TiO_2 layer. In this manner, pits of radii between 5 and 36 nm have been formed in TiO_2 films.

We recently initiated a more detailed experimental and theoretical study of the mechanism of pit formation using the STM tip. Three mechanisms have been considered: (i) dielectric breakdown of the oxide; (ii) chemical etching induced by the electric field; and (iii) mechanical contact between the tip and the surface. Although we have demonstrated that the surface can be damaged by mechanical contact, the data strongly indicate that a voltage bias between the tip and substrate is necessary for the removal of the TiO_2 film. Similar experiments on anodic and native oxides, single crystal TiO_2, and sputtered deposited TiO_2 films on Pt also indicate that the film breakdown is assisted by the electric field between the tip and the TiO_2 film.

We have modeled dielectric breakdown of the oxide film using the system shown in Figure 4. Here, a spherical and electrically charged metal "tip" is positioned directly above a Ti substrate covered by a thin TiO_2 film. The electric potential surrounding the conducting sphere next to the dielectric was built up from solutions to Laplaces equation for a single charge near an infinite grounded dielectric plane. Individual charges were positioned within the sphere until the net potential from each of the charges at a distance R from the center of the sphere was uniform. The potential at any point outside the sphere, according to the supposition principle, was thus obtained by summing the potential from the individual charges. Between the sphere and the top of the dielectric film the components of the field from a single charge in the radial (ρ) and z direction are given by

$$\frac{4\pi R^2\varepsilon_0 E_{1,\rho}}{q} = \rho\left\{(\rho^2+z^2)^{-3/2}-\beta(\rho^2+(2a-z)^2)^{-3/2}-(1-\beta^2)\sum_{n=0}^{\infty}\frac{(-\beta)^n}{(\rho^2+(2a-z+2(n+1)c)^2)^{3/2}}\right\}$$

$$\frac{4\pi R^2\varepsilon_0 E_{1,z}}{q} = \frac{z}{(\rho^2+z^2)^{3/2}} + \frac{\beta\,(2a-z)}{(\rho^2+(2a-z)^2)^{3/2}} + (1-\beta^2)\sum_{n=0}^{\infty}\frac{(-\beta)^n\,(2a-z+2(n+1)c)}{(\rho^2+(2a-z+2(n+1)c)^2)^{3/2}}$$

Within the dielectric the two components are given by

$$\frac{4\pi R^2\varepsilon_0 E_{2,z}}{q} = (1-\beta)\sum_{n=0}^{\infty}(-\beta)^n\left(\frac{-z-2nc}{\sqrt{\rho^2+(z+2nc)^2}} - \frac{2a-z+2(n+1)c}{\sqrt{\rho^2+(2a-z+2(n+1)c)^2}}\right)$$

$$\frac{4\pi R^2\varepsilon_0 E_{2,\rho}}{q} = \rho(1-\beta)\sum_{n=0}^{\infty}(-\beta)^n\left\{[\rho^2+(z+2nc)^2]^{-3/2} - [\rho^2+(2a-z+2(n+1)c)^2]^{-3/2}\right\}$$

where R is the radius of the sphere, q is the magnitude of the charge, ε_0 is the dielectric constant of free space, β is (K-1)/(K+1) where K is the relative dielectric constant $\varepsilon/\varepsilon_0$, ρ is the radial distance from the charge, z is the vertical height with respect to the charge, c is the thickness of the dielectric film, and a is the distance from the charge to the dielectric. ρ, z, c, and a are all normalized to the radius of the sphere, R.

Figure. 4 shows a example of the distribution of the potential between the tip and the substrate, using the appropriate dielectric values of air and TiO_2. The electric field between the tip and underlying substrate was determined using the above equations and compared to literature values of the dielectric strength of TiO_2 to determine the feasibility of dielectric breakdown within the oxide film. Figure 5 shows a comparison of the local electric field (as a function of the tip-to-substrate distance) and the threshold value of the field necessary to cause breakdown of TiO_2. It is clearly evident that the field strength is sufficiently large at close tip-substrate separations (on the order of < 10Å) that dielectric breakdown may occur under the conditions employed in the STM experiments. We have also demonstrated qualitative agreement with the size of the pit (determined by the applied voltage bias) with numerical calculations based on our electric breakdown model. The results of these modeling efforts are currently being written up for publication in which we will delineate the similarities between naturally occurring corrosion mechanisms and STM-induced film breakdown. Ongoing work is described in the Proposed Research.

C) *Correlation of DOS and Oxide Thickness.* In collaboration with Prof. Halley, we have recently begun an investigation of the development of the surface density of electronic states as the oxide is thickened by anodic growth. Figure 6 shows experimental data of the SDOS as a function of the oxide thickness. We observe a monotonic development of the bandgap of TiO_2 as the oxide thickness is increased between its native state (~ 20Å) and 175Å. As in previous measurements of thick films, we observe that the SDOS of thick films indicates a band-gap of ~2eV, which is considerably smaller than the bandgap of bulk TiO_2 (3.04 eV). Equally surprising is the finding that a well defined bandgap is not observed until the film is of the order of ~100Å. The results suggest that the TiO_2 films may be highly disordered in the early stages of growth and that surface vacancies may play a more important role in determining the electronic properties than was previously anticipated. Both possibilities are being investigated by Halley's group in their calculations of the electronic properties of disordered TiO_2 films. In conjunction with these studies, we have also measured the *apparent* barrier heights for electron tunneling, ϕ, for different TiO_2 film thicknesses and at different tip-to-substrate separations, s. Values of ϕ vary considerably with s but are essentially independent of the film thickness. For example, ϕ decreases from ~2 eV to negligible values (i.e., 0 eV) as the distance between the tip and surface is decreased by a few angstroms. The result suggests that at the smallest distances, the tunneling current observed may result from a point contact between the tip and substrate. Conversely, the lack of a dependence of ϕ on the oxide thickness strongly suggests that direct tunneling across the oxide film is insignificant. This finding is particularly important in our interpretation of the unusually large SDOS within the bandgap of native and very thin oxide films.

B) *Quantum Size Effects in Thin Films.* We frequently observe oscillations in the SDOS of native and very thin anodic TiO_2 films which are absent in the SDOS of thicker oxide films (> 50Å). Figure 7 shows a typical example in which 14 clearly defined maxima are observed in the SDOD over a ~4 eV region. These maxima have been tentatively assigned to electron tunneling into quantatized energy states of small oxide-covered Ti particles which are visible in STM images of the surface. A similar phenomenon has been experimentally observed in thin films comprised of small Pt grains and in well-ordered Ag films. We find good agreement between the positions in the SDOS plots with energies predicted from solution of the 1-D Schrodinger equation as shown by the vertical markers in Figure 7. Our interpretation is consistent with the finding that the oscillations disappear with increased oxide thickness which would result in complete oxidation of small metal particles. We also find that the peak positions vary considerably at different positions on the film, a finding that is not surprising in view of the heterogeneity of the surface. This experimental finding is exciting, however, in that it suggests that the electronic structure of thin TiO_2 films may be better described in terms of the collective properties of ultra-fine particles rather than as a continuous film. This interpretation may prove useful in strategies for controlling the electronic and chemical behavior of the surface as well as in interpreting other physical measurements of thin oxide films.

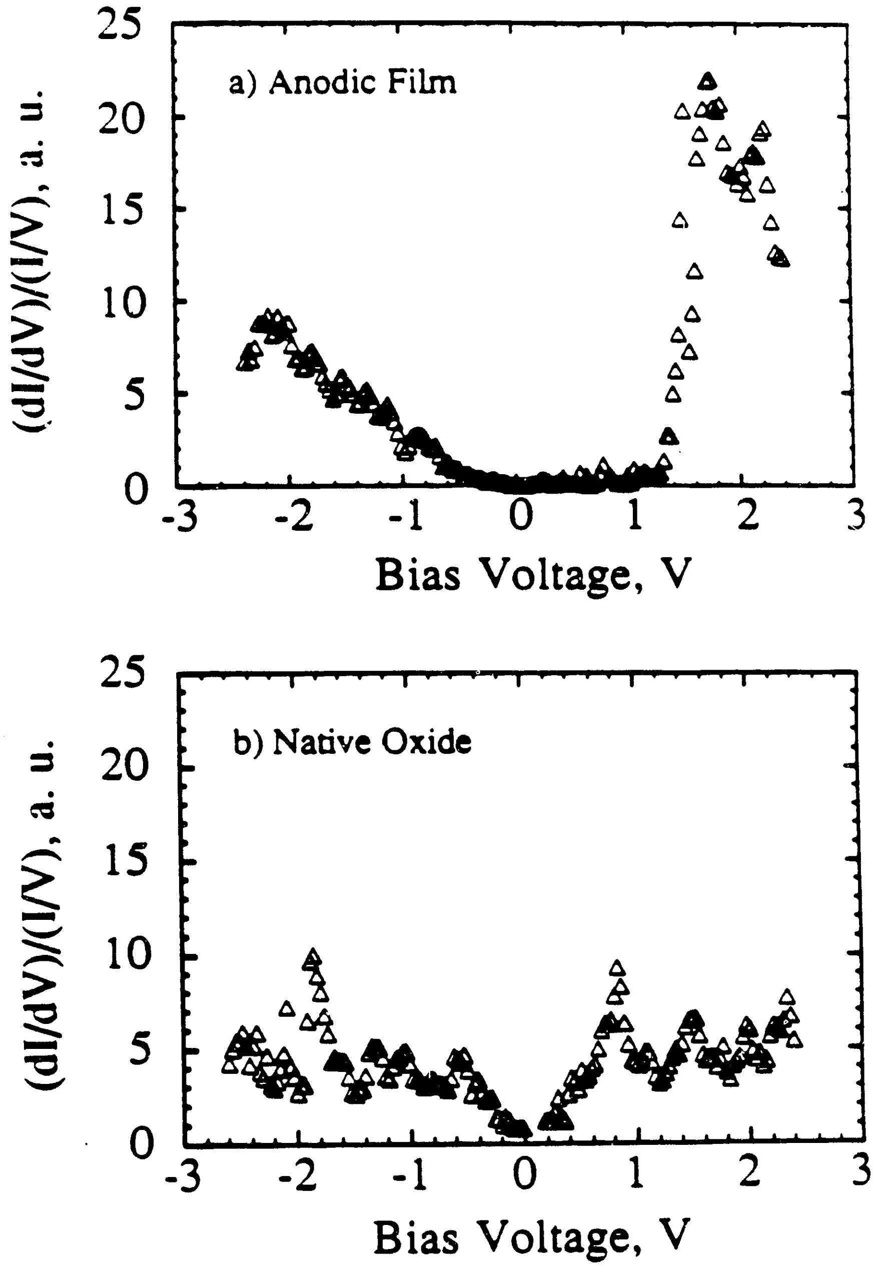

Figure 1. SDOS for a) 160 Å thick and b) native anodically grown TiO_2 films

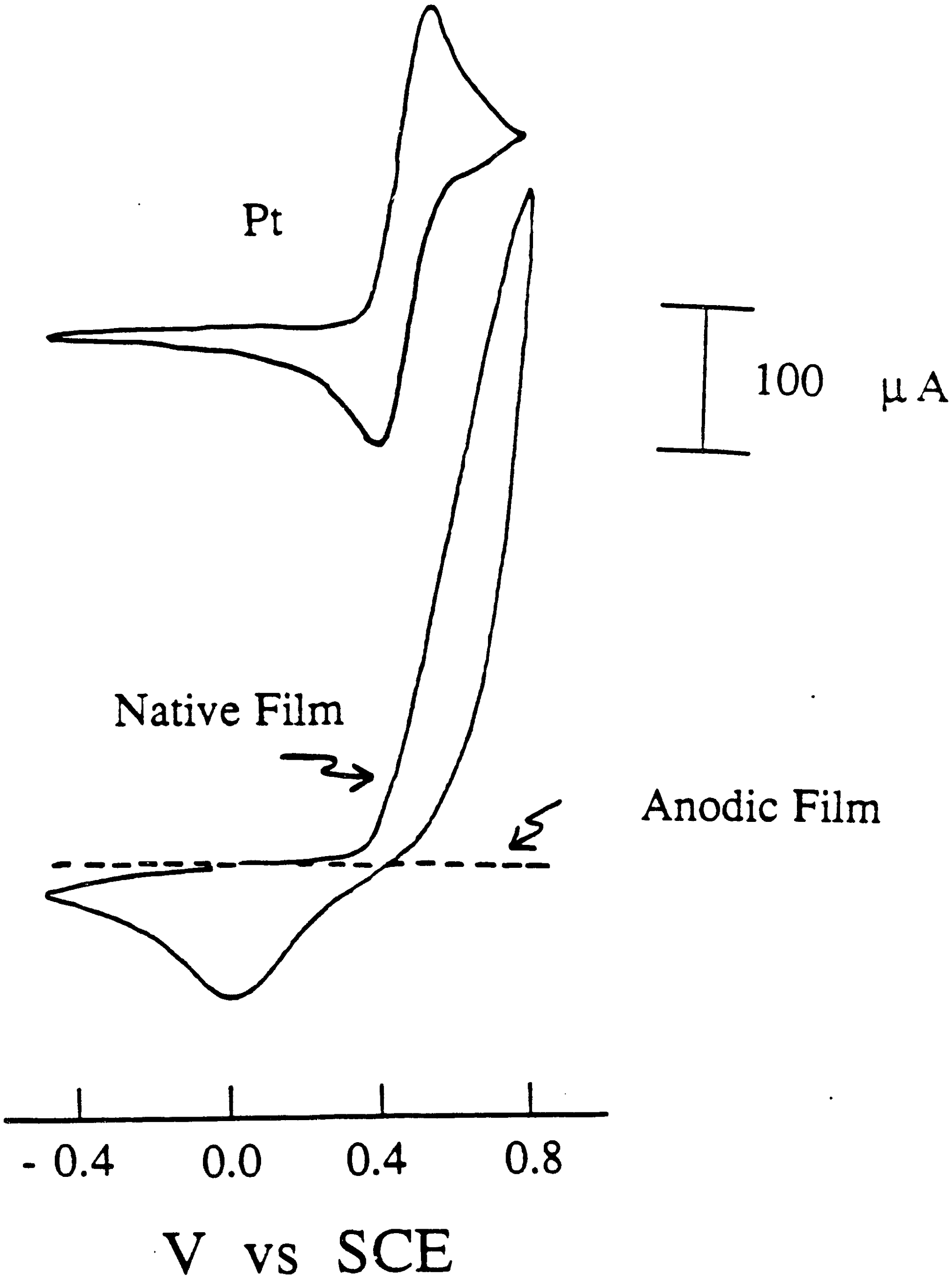

Figure 2. Voltammetric response of native and anodically grown TiO_2 films in CH_3CN solutions containing 5 mM ferrocene as an electron donor. Facile electron-transfer is observed only for the native oxide, consistent with a larger SDOS within the bandgap for the native TiO_2 films (Fig. 1).

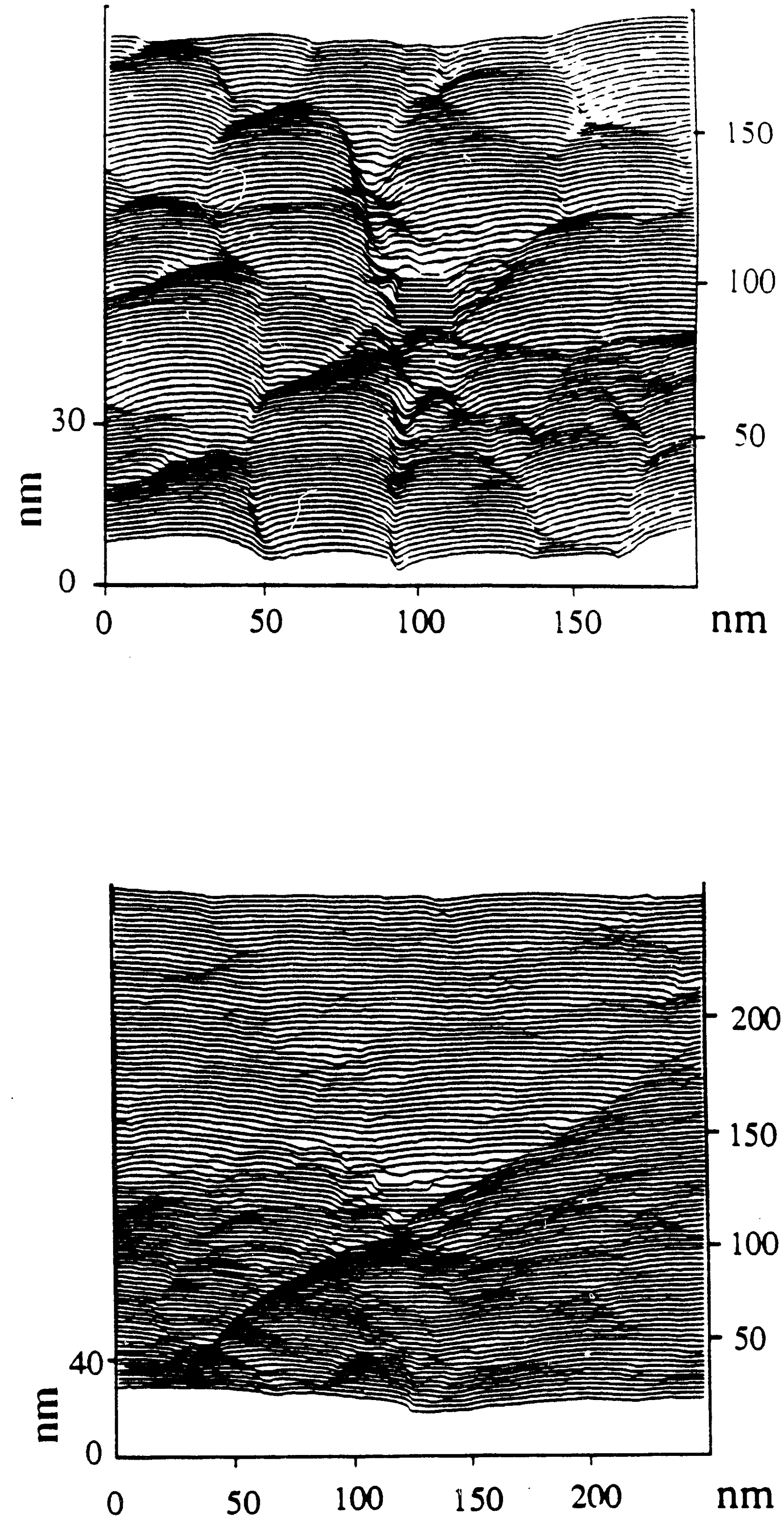

Figure 3. Images of STM-induced (a) a 5 nm radius pit and (b) a ~2 nm wide crack on TiO_2 films.

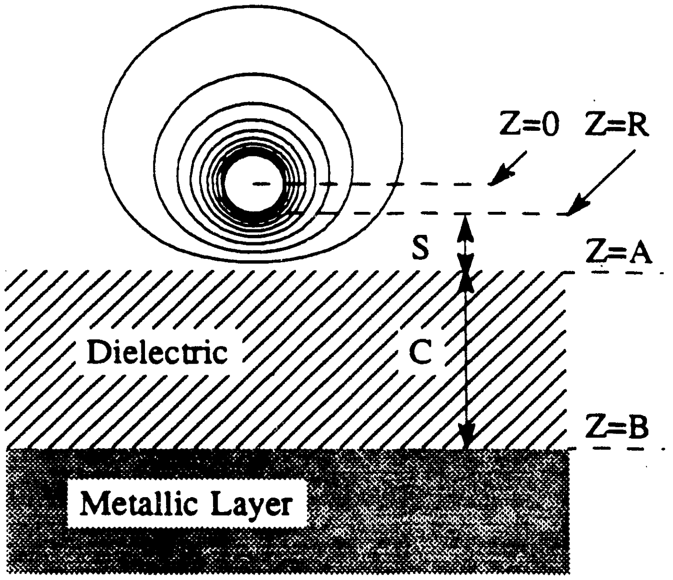

Figure 4. Schematic representation of a conducting sphere of radius R next to a dielectric film of relative dielectric constant K = 70 that is bounded by the planes at Z = A and Z = B. The potential of the sphere is held at voltage V with respect to the bottom side of the dielectric film. The contours surrounding the sphere correspond to equispaced potentials ranging from V (at the surface of the sphere) to 0.05 V at the outermost contour. Dimensions of the sphere, film thickness, and sphere-film spacing are drawn to scale.

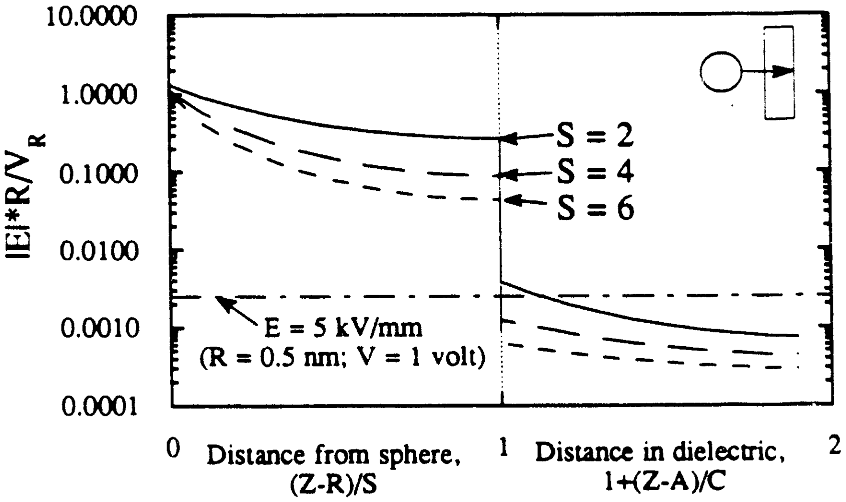

Figure 5. A plot of the variation of the dimensionless electric field along the normal path between the sphere and the dielectric plane. The three curves correspond to different sphere/dielectric spacings, as indicated on the plot, while holding all other parameters as described for Figure 4 constant. The horizontal line corresponds to literature value of dielectric strength of TiO_2 (50,000 V/cm). The dimensionless value of 0.0025 is obtained by assuming a sphere of radius of 0.5 nm with a potential of 1 V.

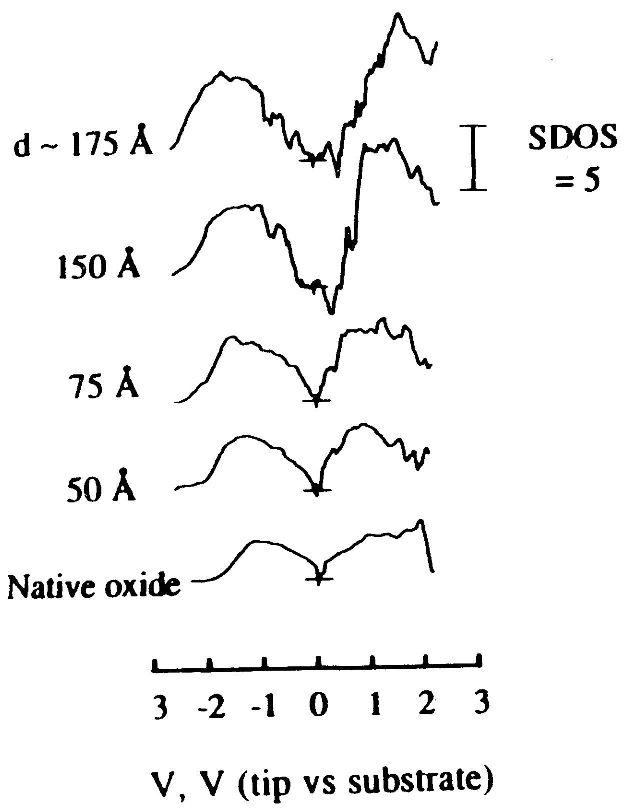

Figure 6. Density of states plots for native and anodically grown TiO_2 films on titanium.

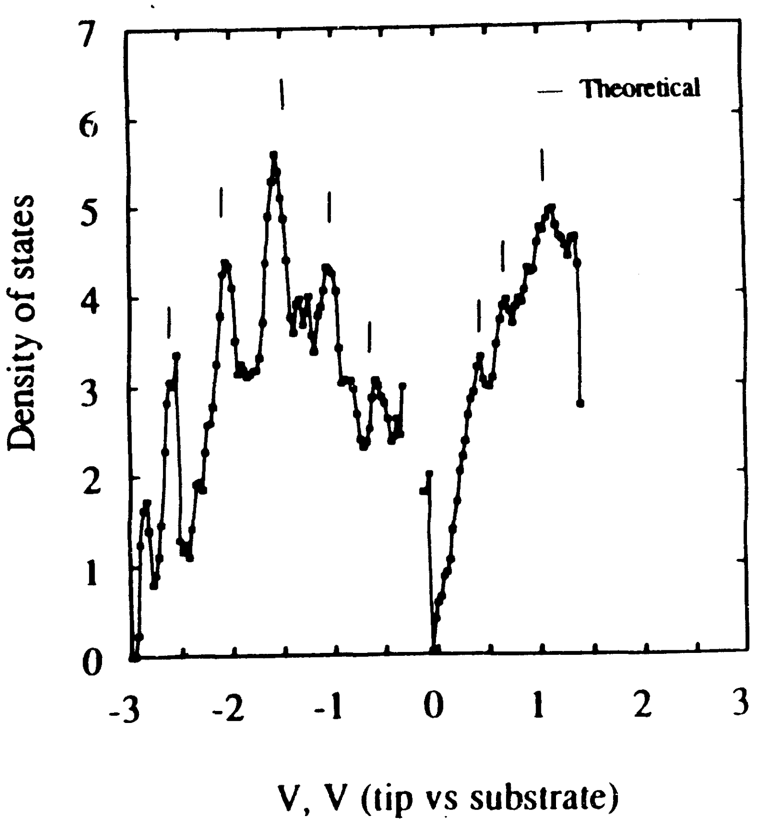

Figure 7. Density of states plot for a native oxide film (< 30 Å) thick compared to theoretical predictions of the allowed energies of electron standing waves within a small metal particle.

V. WORK FUNCTION TOPOGRAPHY ON THIN ANODIC TiO_2 FILMS

R.A. Oriani

1. RESULTS

Work function topography maps of a heterogeneous oxide surface were produced by a scanning Kelvin probe. The specimens studied were anodically grown TiO_2 films on polycrystalline titanium. The defect densities in this oxide vary from one metal grain to another, and this is responsible for the variation of work function with location over the various titanium grains. The Kelvin probe map measures the distribution of surface charge on the oxide surface, a property which influences the catalytic, corrosion, and photoelectrochemical properties of such a surface. These measurements may be extended to other thin oxide films as well.

VI. MODELING OF ELECTRON TRANSFER

J.W. Halley

Research Associate: Xiang Rong Wang

Graduate Student: Yong Joo Rhee (studies completed)

1. RESULTS

Secondly we are studying the temperature dependence of the rate of electron transfer at a metal interface. Research associate Xiang Rong Wang and graduate student Yong Joo Rhee worked on this project which is a collaboration with the corrosion group at Argonne National Laboratory (group leader V. Maroni).

Our work on the activation energy and the transfer coefficient for the temperature dependence and the potential dependence of the ferrous-ferric electron transfer at a gold electrode in two different models was reported in a long paper in the Journal of the Electrochemical Society, written in collaboration with the Argonne group (Curtiss, et al., in press), where the results are compared with experiments carried out by Zoltan Nagy and coworkers at Argonne National Laboratory. A special Cray grant was received to explore our new Lagrange multiplier method (Rhee, 1990) for studying the dynamics near the transition state, applied to the Fe^{2+}-Fe^{3+} problem. We have found preliminary evidence of an unexpected candidate for the transition state in which one water is substantially farther from the iron ion than the other five. Substantial progress has been made on the study of the solvation of the cuprous ion in water. The ion exhibits a Jahn Teller effect which may be important in the Cu^{1+}-Cu^{2+} electron transfer which limits stress corrosion cracking in nuclear reactors in some cases. A preliminary report on our simulation of the Jahn Teller effect for this problem appears in Wang and Halley (1991). (To our knowledge, this is the first simulation of a system exhibiting a Jahn Teller effect in a fluid, and some conceptual issues required clarification before it could proceed.)

VII. STRESS AND HYDROGEN TRANSPORT IN ANODIC FILMS

R.A. Oriani

Graduate Student: John Nelson (studies completed)

1. *RESULTS*

Detailed models for the generation of mechanical stress at and near the interface between a passivating film and its metallic substrate have been formulated. In the case of titanium a large compressive stress produced by electrostriction due to the large electric field across the oxide is exceeded by an even larger tensile stress we have shown that the sign of the non-electrostrictive component of stress is controlled by the magnitude of the transport number, t, for the oxygen ion in the oxide in relation to the critical transport number, t_c, is given by q/(P-BR), where (P-BR) is the Piling-Bedworth ration and q = [volume of metal oxidized - (volume of the cations thus produced)]/(volume of metal oxidized). If $t < t_c$, tensile stress develops; compressive stress develops for $t > t_c$. Our experimental measurements of stress for both Ti and Al anodic oxidation agree with the deductions from the transport numbers found in the literature.

The case of the anodic oxide on nickel is very different. Firstly, it does not have an electrostrictive compressive stress, evidence that the electric field across the nickel oxides is relatively small. Secondly, the compressive stress which is developed by passivation is due to the Piling-Bedworth factor, and the compressive stress decreases with an up-jump of the applied potential and increases with a down-jump of the applied potential. It has been deduced that these changes of stress are due to the cation valence change and the associated change of $OH^-/O^=$ ratio in the oxide caused by the change in applied potential. We have found also that passive films on nickel that are formed in chloride-containing electrolytes have a larger compressive stress than films formed in Cl-free solutions. This is probably due to the larger volume of the Cl-containing oxide, and this in turn may be responsible for the greater ease of pitting of films grown in Cl-containing solutions.

In our studies of hydrogen in passivating films we have found that both the dielectric constant and the donor density of the film on iron are increased by increasing the hydrogen content of the film. The diffusivity of hydrogen in the film on iron also increases with increasing hydrogen content. We have also found that not only increasing anodic potential but also aging the passive film on iron at constant potential increases the mean cationic valence and decreases the proton content of the film.

2. *PROPOSED RESEARCH*

We propose to continue the collaboration with Prof. S.I. Pyun of the Korea Advanced Institute of Science and Technology which has been very fruitful. This collaboration is sponsored by the National Science Foundation, U.S.-Korea Program until 2/29/92, and will be continued informally beyond that date. The experimental work will be done in Korea with initiation, guidance, and interpretation by R.A. Oriani.

The proposed work includes the effect on the mechanical stress in passivating films of

1) The applied anodic potential (and consequently, the effect of rate of film growth and of mean cationic valence)
2) The time (aging) of passivation
3) Jumps between passivating potentials
4) Electrolyte composition, and of changes of electrolyte composition upon a formed passive film
5) Illumination with light of energy above the bandgap energy of the passivating film

The experimental work proposed to be carried out in Minnesota includes the measurement of the rates of achieving steady-state work functions upon switching on, and also off, super-bandgap U.V. illumination over an anodically grown TiO_2 oxide on polycrystalline titanium. The emphasis will be on the variation of these properties with the crystallographic orientation of the underlying metal grains. We will also investigate the variation of work function, with the crystallographic orientation of the underlying metal grains, of anodic oxides on metals other than titanium.

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IX. STUDENT STATUS

Graduate Students Completing Degrees

Yong-Joo Rhee, (PhD - Physics), August 1990, to Department of Chemistry, University of Michigan, Ann Arbor, MI.

John Nelson (PhD - Materials Science), November 1990, Postdoctoral Fellow.

Continuing Graduate Students

Norberto Cassillas, (PhD), Expected Graduation, October 1992.

Johannes H. Sukamto (PhD), Expected Graduation, October 1992.

Chris Smith (PhD)

X. PUBLICATIONS AND PRESENTATIONS

J.W. Halley

Publications

"Electronic Structure of Multiple Vacancies in Rutile TiO_2 by the Equation-of-Motion Method," J.W. Halley, M.T. Michalewicz and N.Tit, Phys. Rev. B **41**, 10165 (1990).

"Dynamical Properties of the Anderson Localization Model in the Short-Time Critical Regime," Phys. Rev. Lett. **66**, 205 (1991).

"Temperature Dependence of the Heterogeneous Ferrous-Ferric Electron Transfer Reaction Rate: Comparison of Experiment and Theory," L.A. Curtiss, J.W. Halley, J. Hautman, N.C. Hung, Z. Nagy, Y.J. Rhee, and R.M. Yonco, J. Electrochem. Soc. (in press, 1991).

"Photoelectrochemical Spectroscopy Studies of Anodic Oxides on Titanium: Theory and Experiment," J.W. Halley, M. Kozlowski, M. Michalewicz, W. Smyrl, and N. Tit, Surface Science (in press, 1991).

"Electronic Properties of Disordered Anodic TiO_2 (001) Surfaces: Application of the Equation-of-Motion Method," N. Tit, J.W. Halley, and M.T. Michalewicz, Surface and Interface Analysis (in press).

Presentations

"The Ferrous-Ferric Electron Transfer Reaction," Physics Department, University of Puerto Rico, J.W. Halley, April 20, 1990.

"Electronic and Solvent Structure of the Metal-Water Interface," Gordon Conference on Water at Interfaces, Meriden, NH, J.W. Halley, July 16-20, 1990.

"Numerical Method for Dynamic Response in Anderson Localization and Related Transport Problems," Localization 1990, Imperial College London, H.B. Shore, August 13-15, 1990.

"The Fractal Geometry of Alloy Dissolution," Materials Science Seminar, Johns Hopkins University, J.W. Halley, November 14, 1990.

"Equation-of-Motion Calculations of Optical Conductivity in Disordered Systems with Application to TiO_{2-x}," N. Tit, J.W. Halley, M.T. Michalewicz, and H. Shore, American Physical Society Meeting, Cincinnati, OH, March 1991.

"New Numerical Methods for the Electronic Defect Structure in Compound Semiconductors," N. Tit, J.W. Halley, American Physical Society Meeting, Cincinnati, OH, March 1991.

"Electronic Properties of Disordered Anodic TiO_2 (001) Surfaces: Application of the Equation of Motion Method," 13th Symposium on Applied Surface Analysis, University of Minnesota, N. Tit, June 12-14, 1991.

Invited talks by J.W. Halley on other topics using similar methods to those used in this work: EPRI Contractors meeting (Palo Alto, June 1990); Materials Science Workshop (Hanoi, VN, October, 1990); Materials Research Society (Boston, MA, December 1990).

Invited talks by J.W. Halley on other topics in physics: NATO Workshop (Exeter, U.K., August 1990); Materials Science Workshop (October 1990, Hanaoi, VN, October 1990).

Symposia: J.W. Halley was on the organizing committee of Many Body VII, to be held in August 1991 at the University of Minnesota. He will organize a symposium on Electronic Structure and Processes at the Electrode-Electrolyte Interface at the Toronto meeting of the ECS in October 1992. He will be joint chairman of the organizing committee for a meeting on quasiparticle excitations in quantum fluids to be held in Eugene, Oregon, in August of 1993.

R.A. Oriani

Publications

"Current transients caused by potential jumps applied to passivating film son nickel," J.C. Nelson and R.A. Oriani, Electrochim. Acta **35**, 1719-26 (1990).

"Interfacial stresses produced by the anodic oxidation of titanium," J.C. Nelson and R.A. Oriani, Proc. 4th Intnl. Corros. Congress, Florence, Italy, Vol. 5, pp. 51-8 (1990).

"Effect of hydrogen on impedance of the passivating film on iron," Rak-Hyun Song, Su-Il Pyun and R.A. Oriani, J. Appl. Electrochem. **21**, 181 (1991).

"Role of hydrogen in the pitting of passivating films on pure iron," Su-Il Pyun, Chan Lim and R.A. Oriani, Corros. Sci., in press.

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