Role of oxygen vacancies in anodic TiO₂ thin films

Nacir Tit^{a,b}, J.W. Halley^b, Marek T. Michalewicz^{b,c} and H. Shore^d

^a International Center for Theoretical Physics, P.O. Box 586, 34100 Trieste, Italy

^b School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455, USA

^c Division of Information Technology, CSIRO, 723 Swanston Street, Carlton, Victoria 3053, Australia

^d Physics Department, San Diego State University, San Diego, California 92182, USA

Received 29 June 1992; accepted for publication 2 October 1992

Defects play an important role in the electronic and optical properties of amorphous solids in general. Here we present both experimental and theoretical investigations on the nature and origin of defect states in anodic rutile TiO₂ thin films (thickness 5–20 nm). There is experimental evidence that the observed gap state at 0.7 eV below the edge of the conduction band is due to an oxygen vacancy. For this reason oxygen vacancies are used in our model. A comparison of the calculated bulk-photoconductivity to photospectroscopy experiment reveals that the films have bulk-like transport properties. On the other hand, a fit of the surface density of states to the scanning tunneling microscopy (STM) on the (001) surfaces has suggested a surface defect density of 5% of oxygen vacancies. To resolve this discrepancy, we calculated the DC-conductivity where localization effects are included. Our results show an impurity band formation at about $p_c = 9\%$ of oxygen vacancies. We concluded that the gap states seen in STM are localized and the oxygen vacancies are playing the role of trapping centers (deep levels) in the studied films.

1. Introduction

Defects play an important role in the electronic and optical properties of amorphous solids in general. They can play a role of trapping centers (deep levels) impeding the conduction as well as dopants (shallow levels) which led investigators (Bardeen, Brattain and Shockley) to the invention of the transistor. To understand their effects, it is essential to know their nature in more detail. In the case of anodic rutile TiO₂ films, the literature suggests [1] that oxygen vacancies and Ti³⁺ interstitials may be among the important defects in the system. Recently, scanning tunneling microscopy (STM) together with tunneling spectroscopy (TS) experiments [2] showed that the gap states at about 0.7 eV below the edge of the conduction band are mainly due to contribution from oxygen vacancies. For this reason we used these vacancies as defects in our calculations and we studied their effects on the electronic properties.

In a previous work [3] we described the equation-of-motion (EOM) method calculations of the electronic structure of perfect and disordered TiO₂(001) surfaces. In the present paper, we describe in detail the origin and nature of the gap states seen in the STM experiment. We attempt to explain both the STM and photospectroscopy experiments and particular attention is paid to understand the role of oxygen vacancies in anodic titanium oxides. In the calculations presented here, we use the EOM method [4], which achieves its efficiency and convenience [5] by avoiding the direct diagonalization of the Hamiltonian in calculating the spectrum of highly disordered solids. We apply this method to a full (sections 2 and 3) and simplified (section 4) tight-binding model developed by Vos [6]. The oxygen vacancy is described by [7] a Yukawa potential and a soft positive core.

In section 2, we describe our calculations of the bulk photoconductivity using the EOM method and we compare our results to the photo-

spectroscopy experiments. We show that the slowly grown anodic TiO₂ films (5 to 20 nm thick) are very close to single crystal rutile in their transport properties. In section 3 we compare our calculated surface density of states (SDOS) to the STM experiments and show that the above films have a disordered electronic structure. To resolve this discrepancy between photospectroscopy and STM experiments, we present in section 4 our calculations of the DC-conductivity, where localization effects are included. In the last section, we summarize our conclusions.

2. Photoconductivity

In an earlier work [8] we reported the calculations of the electronic structure of rutile TiO₂ containing oxygen vacancies. We applied [8] the EOM method to the extensions of the full tight-binding model of Vos [6] to study the density of states as a function of oxygen vacancy concentration and film thickness. For the calculation details we refer the reader to refs [7–9]. The basic approach of the EOM method is to solve the time dependent Schroedinger equation $i\hbar\partial\psi/\partial t = H\psi$ and then to Fourier transform the result in time to obtain the quantities such as the density of states and the conductivity which are of interest at the end of the calculation. For the density of states (DOS), one gets

$$N(E) = \sum_{i,j} \langle i | \delta(E - H) | j \rangle e^{i(\phi_j - \phi_i)}. \quad (1)$$

Where ij denotes sites, ϕ_i is a number chosen at random from the interval $0 < \phi_i < 2\pi$ for each site i , and H is the Hamiltonian of the system. In principle, eq. (1) gives the DOS if one averages the right-hand side over several sets of random phases. Fortunately, the fluctuations in the DOS calculation are also controlled by the size of the system [8] and, hence, a few sets of randomly chosen phases give a very accurate result.

In an experimental work [10] the authors reported photoelectrochemical spectra of anodic oxides grown on polycrystalline titanium substrates. The oxides were grown by potential ramping at 0.1 mV/s, the lowest growth rate reported

in the literature. As the growth rate was increased the oxides became homogeneous and more disordered. The electron diffraction studies [10] showed that the oxides of interest always had a rutile structure. The size of degree of ordering of oxide grains was dependent on the growth rate, substrate crystallography and film thickness. The authors of ref. [10] evaluated the photospectra of the oxide using the simple Butler model [11] (based on the assumption of parabolic band structure) for semiconductor/electrolyte junctions. Their analysis suggested an indirect bandgap of 3.3 eV and a direct bandgap of 3.7 eV for slowly grown oxides (which are of our interest in this article).

In the linear response theory, the photoconductivity of non-interacting electron gas is given by the Kubo–Greenwood formula [12]. We used our density of states results reported in ref. [8] and assumed that all the states contribute to the conductivity [13] (neglect of localization) in evaluating the Kubo–Greenwood formula:

$$\sigma(\omega) = \frac{\text{const}}{\omega} \int_{E_F - \hbar\omega}^{E_F} N(E) N(E + \hbar\omega) dE, \quad (2)$$

where $N(E)$ is the density of states at energy E and E_F is the Fermi energy. This approximation assumes that the matrix elements coupling the light to the electron–hole pairs are independent of the wave vectors of the electron and hole created in the absorption process. To relate the optical conductivity $\sigma(\omega)$ to the quantum efficiency η , we note that [14] the absorption coefficient $\alpha \propto \sigma/c$ (as long as the real part of the dielectric function is varying slowly with ω) and we assume [10] that $\eta \propto \alpha$. We evaluated eq. (2) for samples of size $8 \times 8 \times 10$ unit cells (3840 atomic sites) of TiO₂ containing oxygen vacancies with concentrations 0, 1, 5 and 10%. We included in the calculations 5d orbitals on titanium and 1s and 3p orbitals on oxygen. Periodic boundary conditions were imposed on the system in the directions normal to the c -axis. This model configuration approximates the situation in a TiO₂ film about 3.0 nm thick.

The assumption of parabolic bands, together with the assumption that the photocurrent is pro-

Fig. 1. Comparison of indirect bandgap plots between photo-spectroscopy experiments (crosses) with the EOM method calculations (solid lines) for three films grown to 1.5, 3.5 and 5.5 V (of thickness 50, 120 and 200 Å, respectively). The photospectra were collected under a bias of 1.0 V. The vertical scale is arbitrary.

portional to the absorption coefficient α (i.e. the Butler model) leads to the relation:

$$\eta h\nu = \text{const} (h\nu - E_g)^n, \quad (3)$$

where η is the quantum efficiency and n depends on whether the transition is direct ($n = 1/2$) or indirect ($n = 2$). If eq. (3) is true, then a plot of $(\eta h\nu)^{1/n}$ versus $h\nu$ will provide an x -axis intercept equal to the semiconductor bandgap. Expressing the results as indirect bandgap plots, $(\eta h\nu)^{1/2}$ versus $h\nu$, we show in fig. 1 a comparison between our theoretical results (in solid curves) and the experiments [10] (curves in crosses). The experimental data correspond to films of different thicknesses: 50 Å (final growth voltage of 1.5 V), 120 Å (3.5 V) and 200 Å (5.5 V). However, the theoretical curves correspond to the results of our calculation described above for a sample with no oxygen vacancies. What is significant in fig. 1 is the agreement between theory and experiment at photon energies just above the band edge. (While we have made several assumptions, as discussed above, in computing the solid curves, we emphasize that we have

not assumed that the bands are parabolic near the bandgap.) The bands near the bandgap for our model are almost flat, not parabolic (see Vos' paper [6]). This agreement shows that the energy gap is 3.0 and the assumption of parabolic bands implicit in eq. (2) is not valid here. Hence, the 3.3 eV suggested by the Butler model does not correspond to the bandgap at all. The linear region, which was extrapolated to find the gap could be due to transitions between parabolic bands higher than the bandgap. To draw definite conclusions requires a full group theoretic analysis which we have not undertaken. We deduced from our comparison that the films in interest are very close to bulk rutile in their transport properties with an optical bandgap of 3.0 eV.

3. STM and surface density of states

It is well known [15] that the plots of the dynamic conductance versus the applied bias on the tip, dI/dV versus V , are analogous to the surface density of states (SDOS) plots. It has been a tradition to look at the normalized conductance (ratio of dynamic to static conductances) to suppress the dependence on the tip-surface distance. In fig. 2a we show the experimental results reported by Fan and Bard [2] on an anodic TiO₂(001) surface. This figure reveals that the surface certainly contains defects.

We performed non-self-consistent calculations [3] of the SDOS using the EOM method. Our results [3] on ideal TiO₂(001) surfaces compare favorably with the results of Munnix and Schmeits [16]. Since our method is not self-consistent, we show our results in fig. 2b for comparison on the same energy scale as in fig. 2a. The calculated SDOS shown in fig. 2b is for a sample of size $8 \times 8 \times 2$ unit cell containing 5% oxygen vacancies and under periodic boundary conditions in the directions normal to the c -axis. The results of experiment (fig. 2a) and theory (fig. 2b) are qualitatively similar. The good fit of the donor states suggests that the surface defect density is about $4.74 \times 10^{13} \text{ cm}^{-2}$ (which corresponds to 5% of oxygen vacancies). The difference between figs. 2a and 2b in the shape of the valence and con-

Fig. 2. (a) The normalized conductance as a function of tip voltage for an Ir–Pt tip and an n-TiO₂(001) surface [2]. (b) The solid curve (ii) presents the SDOS normalized to one unit cell (ratio of two Ti sites to four O sites); however, the dotted curve (i) is due to partial contributions from a ratio of two Ti sites to five O sites (to show the local effects seen in STM). The same energy scale as in fig. 2a is shown for comparison.

duction bands is due to several factors. One reason we mention is that the experimental figure includes some local effects: namely the tip sees more oxygen sites than the ratio of our normalized SDOS (4 oxygen atoms to 2 titanium atom). Thus, we also display the SDOS (dotted curve in fig. 2b) which contains a contribution of 5 oxygen sites and 2 titanium sites to show that the local effects can improve the comparison in the continuum regions.

Both STM and tunneling spectroscopy experiments [2] have shown the evidence that gap states on TiO₂(001) surfaces are mainly due to oxygen vacancies. As the growth history of these oxides is

concerned [10], this could be taken in turn as an evidence for existing oxygen vacancies in the bulk of these films.

4. DC-conductivity

To resolve this discrepancy between the photoconductivity (which suggests that the films have bulk-like transport properties) and STM (which suggests disordered electronic structure) experiments, we present calculations of the DC-conductivity, where localization effects are included. In the linear response theory, the DC-conductivity for non-interacting electron gas $T = 0$ K is given by [17] the Kubo–Greenwood formula (when $E_F = E$):

$$\sigma(E) = \frac{2\pi\hbar e^2}{m^2\Omega} \sum_{\mu,\nu} |\langle \mu | P^x | \nu \rangle|^2 \delta(E_\mu - E) \times \delta(E_\nu - E), \quad (4)$$

where the polarization is taken in the direction of the x -axis, α and β label eigenstates, P^x is the momentum operator ($P^x/m = -(i/\hbar)[X, H]$), Ω is the volume of the sample and H is the Hamiltonian of the system. We applied the EOM method on a simplified (2D) tight-binding model of TiO₂ which contains oxygen vacancies with concentrations 1, 5, 8, 9 and 10%. The details of our calculations will appear elsewhere [18]. Special attention in our study is paid to the nature of gap states raising from oxygen vacancies.

The model we study here consists of two layers of TiO₂ with faces normal to the (001) direction. Unlike the DOS calculation, the fluctuations in the DC-conductivity calculation are only controlled by the number of sets of random phases [18]. This makes the latter calculation costly and for this reason we include in our model [18] only one orbital per site (1p orbital per oxygen site and 1d orbital per titanium site). We use a sample of size 40×40 units (1200 sites) with periodic boundary conditions. In fig. 3 we show the total DOS (upper curve) for the sample described above without oxygen vacancies. We show also the contributions from titanium and oxygen sites separately. The gap which we calculate in this

simplified model is (4.24 eV) larger than the bandgap of the full model (3.04 eV). This simplified model, however, is used to illustrate the usefulness of the EOM method to discriminate between extended and localized states (see below).

In fig. 4, we show the effects of including 1, 8 and 10% of oxygen vacancies at randomly selected oxygen sites in the 2D sample described above. The solid lines (i) present the results of DOS and the dotted curves (ii) show the results of DC-conductivity as a function of energy. In the results of DOS, the tail of donor states grows with the oxygen vacancy concentration. There is also an “F-center band” due to states on the oxygen vacancies, lying well above the conduction band as found before [8]. The DC-conductivity results, on the other hand, give information about the localization of the states appearing in the DOS curves (no contribution from localized states). The important features in our results are: (1) We could discriminate between localized and extended states in the DOS. (2) The impurity band forms by a percolation-like process due to the bound state wave function overlap at a threshold concentration p_c of donors (oxygen va-

Fig. 3. Density of states without oxygen vacancies for a 2D-sample of size 40×40 units (1200 sites). The top curve is the total DOS and the remaining curves show contributions from titanium and oxygen sites.

Fig. 4. DOS (upper curve (i)) and DC-conductivity (lower curve (ii)) for a sample of 40×40 units containing oxygen vacancies with various concentrations (1, 8 and 10%). The scale shown is for the DOS in $1/\text{eV}$ units. However, the scales of DC-conductivity are in e^2/h and are equal to the given scale multiplied by: (a) 30, (b) 4.5 and (c) 4.5.

cancies). Taking into account the fluctuations in our method [18], we performed the DC-conductivity calculations for $p = 1, 5, 8, 9$ and 10% of oxygen vacancies to confirm at the end that $p_c = 9.0 \pm 0.2\%$ of oxygen vacancies. (3) For defect densities below this threshold ($p < p_c$) the functional form of the conductivity and the mobility edge are almost invariant. (4) As the oxygen vacancy concentration increases the conductivity shrinks. More details about the nature of localization will appear elsewhere [18].

We also performed local density of states (LDOS) calculations on several sites around the vacancy to study the behaviour of the bound-state and F-center wavefunctions. We approximate [19] the decay of the bound-state intensity as $\rho = \rho_0 \exp(-x^2/2L^2)$, where L is the decay length of the bound-state wave function. As the bound states in the gap are associated to titanium sites, we calculated the LDOS on two different titanium sites around the vacancy to estimate $L \cong$

Fig. 5. The spatial decay of the bound-state (curve (i)) and F-center (curve (ii)) wave function amplitudes.

$2.13 \text{ \AA}$ using the above function. In fig. 5 we show the spatial decay of the bound state in solid curve (i). In order that the impurity band forms, it is necessary that the bound-state wave functions overlap from one defect to another. Hence, we estimated the threshold of impurity band appearance to $p_c \approx 9\%$, which is consistent with our DC-conductivity results shown above. Hence, our results show that the gap states are localized for $p < 9\%$ of oxygen vacancies. We deduced that the studied films have oxygen vacancies with concentrations lower than the threshold of impurity band formation.

5. Conclusions

We have shown that the slowly grown anodic TiO_2 films have oxygen vacancies with a concentration lower than the threshold of impurity band formation. As a consequence the gap states raising from oxygen vacancies (as seen in STM experiments) are localized in agreement with photo-spectroscopy experiment. We concluded that the oxygen vacancies are playing the role of trapping

centers (deep levels) impeding the electronic conduction in these films.

Acknowledgements

One of us (N.T.) thanks Professor Abdus Salam and the IAEA for their hospitality at the International Center for Theoretical Physics in Trieste. This work was supported in part by the Department of Energy (grant DE-FG02-91-ER45455) and the Minnesota Supercomputer Institute.

References

- [1] P.F. Chester, J. Appl. Phys. 32 (1961) 2233.
- [2] F.F. Fan and A.J. Bard, J. Phys. Chem. 94 (1990) 3761.
- [3] N. Tit, J.W. Halley and M.T. Michalewicz, Surf. Interf. Anal. 18 (1992) 87.
- [4] R. Alben, M. Blume, H. Hrakauer and L. Schwartz, Phys. Rev. B 12 (1975) 4090.
- [5] N. Tit and J.W. Halley, Phys. Rev. B 45 (1992) 5887.
- [6] K. Vos, J. Phys. C 10 (1977) 3917.
- [7] J.W. Halley and H. Shore, Phys. Rev. B 36 (1987) 6640.
- [8] J.W. Halley, M.T. Michalewicz and N. Tit, Phys. Rev. B 41 (1990) 10165.
- [9] M.T. Michalewicz, H. Shore, N. Tit and J.W. Halley, Comput. Phys. Commun. 71 (1992) 222.
- [10] M.R. Kozlowski, P.S. Tyler, W.H. Smyrl and R.T. Atanasoski, Surf. Sci. 194 (1988) 505.
- [11] M.A. Butler, J. Appl. Phys. 48 (1977) 1419.
- [12] N.F. Mott and E.A. Davis, in: Electronic Processes in Non-Crystalline Materials (Clarendon, Oxford, 1971) p. 10.
- [13] J.W. Halley, M. Kozlowski, M. Michalewicz, W. Smyrl and N. Tit, Surf. Sci. 256 (1991) 397.
- [14] J.D. Jackson, in: Classical Electrodynamics, 2nd ed. (Wiley, New York, 1975) p. 286.
- [15] R.M. Feenstra, J.A. Stroscio and A.P. Fein, Surf. Sci. 181 (1987) 295.
- [16] S. Munnix and M. Schmeits, Phys. Rev. B 30 (1984) 2202.
- [17] C.M. Soukoulis and E.N. Economou, Phys. Rev. Lett. 52 (1984) 565.
- [18] J.W. Halley, H. Shore and N. Tit, to be published.
- [19] E.N. Economou, in: Green's Functions in Quantum Physics, Ed. P. Fulde (Springer, Berlin, 1983) p. 102.