

Surface photovoltage spectroscopy study of reduced and oxidized nanocrystalline TiO₂ films

A. Rothschild^{a,*}, A. Levakov^b, Y. Shapira^b, N. Ashkenasy^{b,1}, Y. Komem^a

^a Faculty of Materials Engineering, Technion—Israel Institute of Technology, Technion City, Haifa 32000, Israel

^b Department of Electrical Engineering—Physical Electronics, Tel Aviv University, Tel Aviv 69978, Israel

Abstract

Nanocrystalline TiO₂ films used for gas sensors have been studied by means of surface photovoltage spectroscopy and other analytical tools to investigate the oxygen chemisorption effect on the electrical properties of the films. The results show that the surface (and intergranular interface) band bending increases with oxygen exposure due to electron trapping at midgap states induced by chemisorption. The surface electronic structure is revealed by the measurements, allowing determination of the sensing mechanism of these important films. In addition, a photoinduced chemisorption of oxygen at room temperature is observed. This has important implications for low-temperature gas sensors.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Titanium oxide; Polycrystalline thin films; Surface electronic phenomena (work function, surface potential, surface states, etc.); Surface photovoltage; Chemisorption; Interface states

1. Introduction

Nanocrystalline titanium dioxide (TiO₂) has many important applications such as solar cells [1], photocatalysts for water photolysis [2] and degradation of environmental pollutants in air and wastewaters [3,4], and as an oxygen- and gas-sensor material [5]. The key mechanisms in these applications are based on surface redox reactions that lead to charge separation in the space-charge region adjacent to the surface and/or charge transfer between the surface and the bulk of the

nanosized crystallites [6]. Thus, it is important to understand the impact of such reactions on the electronic properties of nanocrystalline TiO₂.

TiO₂ forms three different crystalline structures: rutile, anatase, and brookite. Rutile is the thermodynamically stable phase, while anatase and brookite are metastable polymorphs that irreversibly transform to rutile upon heating [7]. The electronic structure and properties of single-crystalline rutile have been studied quite extensively (see, e.g., Refs. [8–10]), but only little is known on nanocrystalline rutile [11], while most of the literature on nanophase TiO₂ concerns ultra fine colloids of the anatase modification (see, e.g., Refs. [12,13]). The interest in colloidal anatase stems from its high photocatalytic activity, which is considered by many to be superior to that of rutile [3,4]. However, the rutile phase is much more stable than anatase and easier to produce. In fact,

* Corresponding author. Tel.: +972-4-8294598; fax: +972-4-8321978.

E-mail address: mtavner@tx.technion.ac.il (A. Rothschild).

¹ Present address: The Scripps Research Institute, La Jolla, CA 92037, USA.

thin films of TiO₂ produced by reactive sputtering on oxidized Si substrates for gas sensing applications were found to transform to polycrystalline rutile upon heating to 400 °C or above [14]. In this paper we present a comparative surface photovoltage spectroscopy (SPS) study of reduced and oxidized TiO₂ rutile films used for gas sensors [14], and discuss the effects of oxygen exposure on their electronic properties.

2. Experimental

Thin films of TiO₂ (~200 nm) were deposited on oxidized Si(1 0 0) substrates by reactive sputtering, as described elsewhere [14]. For the SPS measurements the TiO₂ films were deposited on a thin Au layer covering the Si substrate to provide back contact for the Kelvin probe apparatus. After deposition, all samples were annealed at 450 °C in a vacuum of ~10⁻⁷ mbar for 24 h in order to crystallize the films and stabilize their microstructure. Afterwards, some samples were reduced (again) by annealing under high vacuum (~10⁻⁷ mbar) at 450 °C for 24 h, while others were oxidized by annealing in dry atmospheric air at 400 °C for 24 h. Microstructural characterization of the films was carried out using X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution scanning electron microscopy (HRSEM). The chemical composition was examined by Rutherford backscattered spectroscopy (RBS). The electronic properties of the films were investigated by means of SPS measurements [15]. The measurements were conducted inside a dark Faraday cage, in atmospheric air at room temperature. The contact potential difference (CPD) was monitored using a commercial Kelvin probe unit (Besocke Delta Phi, Germany) with an Au probe, providing ~1 mV sensitivity. The samples under investigation were illuminated through a double 0.25 m grating monochromator fed by a 150 W Xe lamp. The output illumination power at the sample surface typically lied in the μW range, covering the entire probe area (2.5 mm in diameter). Prior to illumination, each TiO₂ sample was maintained in the dark for 24 h in order to eliminate persisting effects of previous light expo-

sure. Wavelengths were scanned from 1000 to 250 nm, in 0.1 nm steps and with a dwell time of 1 s between each step.

3. Results

After the initial thermal treatment (450 °C at ~10⁻⁷ mbar for 24 h) the TiO₂ films had a polycrystalline rutile structure that did not change upon subsequent annealings [14]. The crystallized films were columnar, with grain diameter between 10 and 80 nm (with an average of ~36 nm), as shown in the plan-view TEM micrograph in Fig. 1(a). The height of the columnar grains was the same as the film thickness, as shown in the cross-section TEM micrograph in Fig. 1(b). RBS measurements indicated the O/Ti ratio was about 2:1, and no impurities except for Ar were detected.

Fig. 2 shows CPD spectra of two identical TiO₂ samples (from the same deposition batch). One sample (top) was reduced by annealing under high-vacuum conditions (~10⁻⁷ mbar), while the other sample was oxidized in dry atmospheric air (bottom).

4. Discussion

The CPD spectra of both the reduced and oxidized TiO₂ films (Fig. 2) show a decrease in the CPD upon super-band gap illumination ($h\nu > 3$ eV), indicating that both films are n-type semiconductors [15]. The most striking difference between the two spectra is the magnitude of the surface photovoltage (SPV). The maximum SPV of the oxidized sample is ~340 mV, while that of the reduced sample is only ~90 mV. This indicates that the (upwards) surface band bending is much stronger in the oxidized film than in the reduced film [15]. This is attributed to chemisorption of oxygen anions during the annealing in an oxygen-rich atmosphere (air) [14,16]. Therefore, the surface and interface (i.e., grain boundary) band bending is much stronger in the oxidized film than in the reduced film, and consequently its SPV is larger. Fig. 2 shows that the dark CPD of the reduced TiO₂ film is higher by ~40 mV than that of

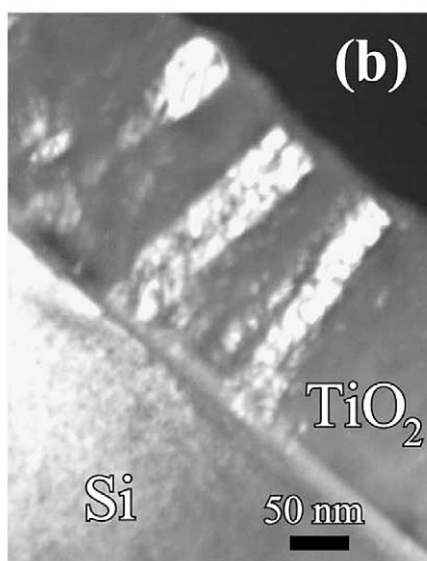
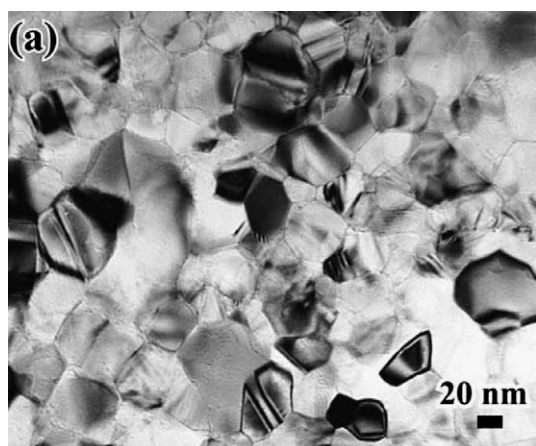


Fig. 1. TEM micrographs of a typical TiO_2 film: (a) a plan-view micrograph (bright field); (b) a cross-section micrograph (dark field).

the oxidized film. The dark CPD is the difference between the work functions of the semiconductor (W_S) and the Kelvin probe metal electrode (W_M) [15]. $W_S = \zeta - eV_s + \chi - \Delta\phi_s$, where ζ is the difference between the conduction band edge E_C and the Fermi level E_F in the semiconductor bulk, e is the electron charge, V_s is the surface potential, χ is the electron affinity, and $\Delta\phi_s$ is the surface dipole energy [15]. Thus, $W_S(\text{reduced film}) - W_S(\text{oxidized film}) \approx 0.04$ eV (in the dark). From the oxygen

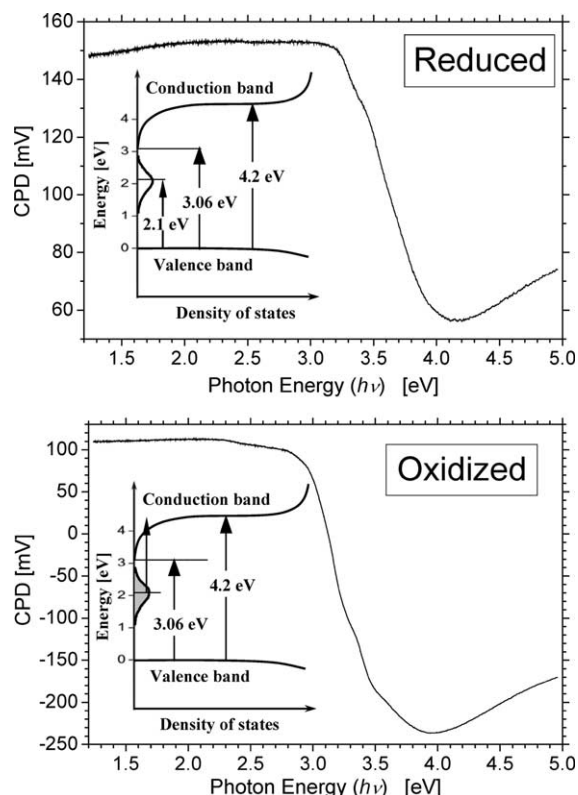


Fig. 2. CPD spectra of two TiO_2 samples reduced by annealing in high vacuum (top) or oxidized by annealing in atmospheric air (bottom). The inserts show the schematic electronic structure, as discussed in the text.

pressure dependence of the carrier concentration in TiO_2 , $n \propto (p_{\text{O}_2})^{-1/6}$ [17], we estimate $\zeta(\text{reduced film}) - \zeta(\text{oxidized film}) \approx -0.1$ eV, and from the SPV we get $eV_s(\text{reduced film}) - eV_s(\text{oxidized film}) \geq 0.25$ eV ($eV_s < 0$ in both cases since the bands are bent upwards). Assuming that the electron affinity χ is about the same for both films, we deduce that the surface dipole energy of the reduced film must be more negative by ~ 0.39 eV than that of the oxidized film. This can be attributed to chemisorption of water molecules, which is much stronger at reduced $\text{TiO}_{2-\delta}$ surfaces than at stoichiometric TiO_2 surfaces because it requires surface oxygen vacancy defects that act as active adsorption sites [10]. At room temperature H_2O adsorbs dissociatively on reduced rutile surfaces, forming OH^- species pointing outwards of the surface [10]. The coverage of OH^- adsorbates at

reduced rutile surfaces can be as high as one monolayer, whereas stoichiometric surfaces are nearly inert to water chemisorption [10]. This can explain the remarkable difference in the surface dipole energy between the reduced and oxidized films: assuming a dipole length of ~ 2 Å and a coverage of one monolayer of OH^- adsorbates, $\Delta\phi_s \approx -0.36$ eV may be estimated for the reduced film.

In addition to the differences in the SPV and the dark CPD values, there is also a considerable difference in the structure of the CPD spectra of the reduced and oxidized films. Since the photoinduced changes in the CPD spectra, i.e., the SPV, arise from electronic transitions followed by charge redistribution within the space-charge region, which occur when photons with sufficient energy ($h\nu$) are absorbed [15,18], it is useful to divide the spectra into two regimes: (i) the sub-band gap regime, for photon energies below the fundamental absorption edge (FAE) of TiO_2 ; (ii) the super-band gap regime, for photon energies above the FAE. The FAE of rutile is at $h\nu = 3.06$ eV at room temperature, corresponding to a forbidden direct transition [8], while the first absorption peak occurs at $h\nu \approx 4.2$ eV, corresponding to the first allowed direct transition [9].

In the sub-band gap regime ($h\nu < 3$ eV), the CPD of the reduced film shows a gradual slight increase right from the lowest photon energies and up to $h\nu \approx 2.1$ eV, at which point the CPD ceases to change until about 3 eV. The spectrum of the oxidized film demonstrates an opposite behavior, which is attributed to chemisorption-induced surface states distributed in energy around the mid-gap of the allowed band-to-band transition, i.e., centered ~ 2.1 eV above the valence band maximum. Thus, the reduced sample, which is nearly devoid of charged oxygen chemisorbates (occupied surface states) prior to the measurement, starts to adsorb oxygen anions upon illumination during the CPD spectrum measurement, which is carried out in atmospheric air. As a result, conduction band electrons become localized (captured) in chemisorption-induced surface states, and due to this population of the surface states the CPD increases up to a maximum [15,18]. When the incident photon energy exceeds ~ 2.1 eV, the rates of

surface state population (electron capture) and depopulation (electron emission from the states into the conduction band) become the same, and therefore the CPD does not change any more. The opposite scenario occurs in the oxidized film, which is saturated with chemisorbed oxygen anions. Thus, band gap states below E_F are already occupied, and therefore the CPD is constant for $h\nu < 2.1$ eV. Only when the incident photon energy exceeds the minimum energy required for transferring electrons from the surface states into the conduction band the CPD starts to decrease.

In the super-band gap regime the CPD spectra of the reduced and oxidized films are quite similar, except for the difference in the SPV magnitude. In addition, the features in the spectrum of the oxidized film are red-shifted by ≈ 0.2 eV with respect to the same features in the spectrum of the reduced film. Thus, the initiation of the steep fall is at $h\nu \approx 2.9$ and 3.1 eV, respectively (see Fig. 2). This red shift may be attributed to excitons [19], which dissociate to free electrons and holes in the oxidized film due to the high internal electric field in this film. Therefore, the SPV starts to increase at lower photon energies than the FAE (corresponding to the binding energy of the excitons). Another possible explanation for this phenomenon is the band tailing effect in polycrystalline semiconductors with electrically active (i.e., charged) grain boundaries [20]. The minima in the CPD spectra of the films arise from the saturation of the SPV when the first allowed direct transition occurs. At higher photon energies the CPD gradually increases, which is probably due to a decrease in the incident illumination intensity close to its spectral limit.

5. Conclusions

SPS measurements of reduced and oxidized nanocrystalline TiO_2 films revealed the effect of oxygen chemisorption on the electronic properties of the films. The SPV of the oxidized film was much higher than that of the reduced film. This is attributed to chemisorbed oxygen anions that induce gap states centered at about 2.1 eV above the valence band maximum. These states at the

crystallites surfaces and intergranular interfaces (i.e., grain boundaries) capture conduction band electrons, producing depletion layers in the adjacent regions and surface and intergranular potential barriers. Consequently, the surface conductivity and the intergranular conductivity decrease upon exposure to oxygen, which explains the oxygen sensing mechanism of these films at elevated temperatures (at high temperatures, i.e., above ~ 600 °C, bulk effects are expected to dominate). In addition, it was found that photoinduced chemisorption of oxygen occurs in reduced TiO_2 films at room temperature. This effect might be of great importance for gas sensor applications because it means that with appropriate illumination the operating temperatures may be decreased.

Acknowledgements

The authors wish to thank Prof. Frederic Cosandey (Rutgers University) for supplying the TiO_2 samples for this study. YS is grateful to Dinah and Henry Krongold for their generous support. YK is grateful for the Fund for the Promotion of Research at the Technion for partial support.

References

- [1] M. Grätzel, *Nature* 414 (2001) 338.
- [2] A. Fujishima, K. Honda, *Nature* 238 (1972) 37.
- [3] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 98 (1995) 69.
- [4] A.L. Linsebigler, G. Lu, J.T. Yates Jr., *Chem. Rev.* 95 (1995) 735.
- [5] M.J. Madou, S.R. Morrison, *Chemical Sensing with Solid State Devices*, Academic, San Diego, 1989.
- [6] T. Gerfin, M. Grätzel, L. Walder, *Prog. Inorg. Chem.* 44 (1997) 345.
- [7] J.L. Murray, H.A. Wriedt, in: J.L. Murray (Ed.), *Phase Diagrams of Binary Titanium Alloys*, ASM, Ohio, 1987, pp. 211–227.
- [8] J. Pascual, J. Camassel, H. Mathieu, *Phys. Rev. Lett.* 39 (1977) 1490; J. Pascual, J. Camassel, H. Mathieu, *Phys. Rev. B* 18 (1978) 5606.
- [9] A. Amtout, R. Leonelli, *Phys. Rev. B* 51 (1995) 6842.
- [10] V.E. Henrich, P.A. Cox, *The Surface Science of Metal Oxides*, Cambridge, Cambridge, 1994, pp. 181–192, 316–333.
- [11] M. Anpo, T. Shima, S. Kodama, Y. Kubokawa, *J. Phys. Chem.* 91 (1987) 4305.
- [12] R. Könenkamp, *Phys. Rev. B* 61 (2000) 11057.
- [13] S.A. Bilmes, P. Mandelbaum, F. Alvarez, N.M. Victoria, *J. Phys. Chem. B* 104 (2000) 9851.
- [14] A. Rothschild, F. Edelman, Y. Komem, F. Cosandey, *Sens. Actuators B* 67 (2000) 282.
- [15] L. Kronik, Y. Shapira, *Surf. Sci. Rep.* 37 (1999) 1; L. Kronik, Y. Shapira, *Surf. Interf. Anal.* 31 (2001) 954.
- [16] W. Göpel, G. Rucker, R. Feierabend, *Phys. Rev. B* 28 (1983) 3427.
- [17] P. Kofstad, *Nonstoichiometry Diffusion and Electrical Conductivity in Binary Metal Oxides*, Krieger, Malabar, 1983, pp. 143–145.
- [18] H.C. Gatos, J. Lagowski, *J. Vac. Sci. Technol.* 10 (1973) 130.
- [19] K.W. Böer, *Survey of Semiconductor Physics*, Van Nostrand Reinhold, New York, 1990, pp. 365–394.
- [20] J. Werner, W. Piesl, *Phys. Rev. B* 31 (1985) 6881.