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Sensitization of Polycrystalline $SrTiO_3$ Photoanodes by Mechanical Polishing

B. T. CHANG,[1] G. CAMPET, J. CLAVERIE, AND P. HAGENMULLER
Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex, France

AND J. B. GOODENOUGH
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, Great Britain

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The photoelectrochemical properties of polycrystalline $SrTiO_3$ anodes have been investigated as a function of surface treatment. Mechanical polishing of the undoped samples results in an anomalous visible photoresponse extending to 600 nm. The polishing effect can be removed by either chemical etching or annealing of the samples. An energy diagram of the polished undoped $SrTiO_3$ electrode and the main mechanism of its visible photoresponse have been proposed.

Introduction

Photoelectrochemistry is presently enjoying a period of significant development in both theory and applications (*1, 2*). Photoelectrochemical systems have shown an excellent capability to perform the three functions required for photochemical conversion and storage of solar energy, namely:

(i) efficient absorption of sunlight to produce electrons and positive holes,

(ii) efficient separation and stabilization of the photogenerated positive and negative carriers,

(iii) efficient subsequent redox chemistry to yield oxidized and reduced chemical species.

In fact an AM1 (100 $mW \cdot cm^{-2}$) solar-to-electrical conversion efficiency of 12% has been reported for the n-GaAs $|K_2Se$–K_2Se_2–KOH|C semiconductor liquid-junction photovoltaic cell for a period corresponding to the passage of 35,000 $C \cdot cm^{-2}$ (*3*).

On the other hand, no semiconducting electrodes having all the characteristics required for the decomposition of water into hydrogen and oxygen by sunlight, has yet been found. Up to now, no semiconducting material exhibits both high conversion efficiency and long-term stability. Attempts to overcome this problem include:

(i) development of new semiconducting oxides and layered chalcogenides (*2, 4–6*),

(ii) photosensitization by bulk or surface doping of large band-gap, but stable semiconducting electrodes (*7–16*),

(iii) use of aqueous suspensions of semi-

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[1] Permanent address: Korean University, Kodaira 167 Tokyo, Japan.

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conducting titanate particles that behave as microelectrolytic cells (*1, 17–25*).

Semiconducting metal oxides are generally favored as oxygen photoelectrodes; they are the most stable materials against photocorrosion in aqueous electrolytes. Besides stability, the ideal photoanode must combine a band-gap energy small enough ($E_g < 2.4$ eV) for the capture of significant part of the sunlight and an electron affinity low enough for the photogenerated electron-hole pairs to be spontaneously separated under load conditions.

Figure 1 shows a correlation between the flat-band potential vs standard hydrogen electrode (SHE) and the band-gap energy for several oxides; the flat-band potential is seen to become more positive as the band-gap decreases (*26*). The energy of the top of the $O^{2-}:2p^6$ band does not vary significantly, and only semiconductors having a large band-gap are able to drive spontaneously the photodecomposition of water into hydrogen and oxygen. Although n-type materials can be chosen to give a desired flat-band potential, strategies to simultaneously introduce a valence band above the top of the $O^{2-}:2p^6$ bands have so far been unsuccessful.

Among the stable semiconducting photoanodes having a small electron affinity, $SrTiO_3$ is the most commonly used (*27–38*). It has an empty $3d$ conduction band with an edge about 0.6 V above the H^+/H_2 level in the aqueous electrolyte ($p_H = 0$), but the $O^{2-}:2p^6$ valence band lies too far below the O_2/H_2O level for photoelectrolysis with sunlight.

A method to overcome the lack of absorption in the visible, due to too large an energy gap (3.2 eV), is to introduce donor levels such as $Cr^{3+}:3d^3$ into the gap of Sr TiO_3 (*8, 39–44*). Electrons can be excited by visible light from those levels into the $Ti^{4+}:3d$ conduction band. However, the oxidized chromium ions act as recombination centers for the electrons of the conduction band (*40*); therefore, too high a concentration of Cr^{3+} reduces drastically the electronic mobility and consequently the efficiency of the electrode (*45*). It is difficult therefore, to get an efficient photoresponse to visible light at small applied potentials by the substitution of Ti in $SrTiO_3$ with other transition metal ions, even if this substitution is confined to the surface depletion layer (*42–44*).

An alternative approach is to introduce band-gap states into the depletion layer via lattice defects produced by specific surface treatments of the anode.

Experiments on the photoelectrolysis of water with n-TiO_2 and n-$SrTiO_3$ anodes, have suggested the existence of surface states located near the middle of the band-gap of the materials in order to account for the high electron quantum efficiencies observed in the uv region (*46, 47*). The charge-transfer process at the interface between the semiconductor and the electrolyte, could occur quite efficiently via surface states located close to the O_2/H_2O level. Laser and Gottesfeld showed that a visible photocurrent could be measured for TiO_2-film electrodes produced by thermal oxidation of a Ti metal rod: the authors interpreted the results in terms of photoinduced transfer to and from active band-gap states located at or close to the surface (*48*). Wilson *et al.* investigated the photoelectrochemical behavior of single-crystal TiO_2 electrodes as a function of electrode preparation; they found that mechanical polishing of the electrodes induced a disturbed layer about 1 μm deep that had an important influence on the electrode properties (*49*). From nonlinear Mott-Schottky plots for TiO_2 electrodes, Nagomi has pointed out that mechanical polishing of the samples results in an increase in thickness of an interface layer having a distributed density of band-gap states (*50*).

In this paper, we investigate the influence of specific surface treatments upon the pho-

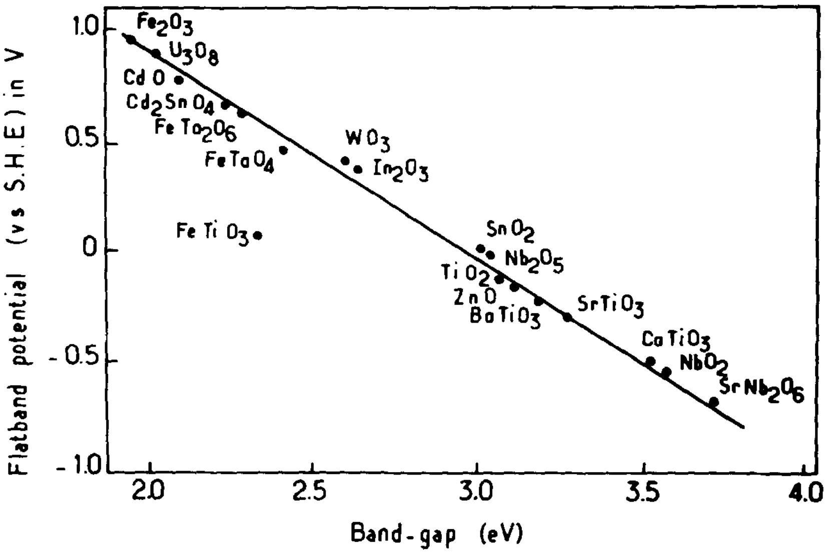


FIG. 1. Correlation between flat-band potentials and band-gaps of semiconducting oxides (*26*).

toelectrochemical properties of undoped $SrTiO_3$ anodes.

Experimental

Anode preparation. The starting materials were $SrCO_3$ and TiO_2. All were purchased from Merck and were 99.99% pure or better (optically pure). The reactants were finely ground and dehydrated before weighing. They were then mixed intimately in an agate mortar, calcined at 1350°C and then pelletized. The pellets (5 mm diameter, 1–2 mm thickness) were sintered at 1400°C for 15 hr so as to achieve good compactness capable of giving reproducible results. The samples were then reduced under flowing hydrogen, at 1350–1400°C for 24 hr, to make the materials n-type. The resistivities of the samples were less than $90\ \Omega \cdot \text{cm}$.

Surface treatment of the pellets. Four different surface treatments have been used; their identification is given in parentheses:

(i) Mechanical polishing with SiC emery paper of 12 μm roughness (pol.).

(ii) Etching in concentrated nitric acid (12 *N*) at 120°C for 5 min (et.).

(iii) Polishing, then etching (pol.-et.).

(iv) Polishing, then reheating in H_2 at 1300°C for 10 hr (pol.-heat.).

After surface treatment, the pellets were carefully rinsed in distilled water and acetone, then dried. We checked by X-ray fluorescence analysis and Auger spectroscopy seeing that no detectable impurity of any kind had been introduced into the samples during the surface treatment procedures.

Electrode preparation. After a given surface treatment, ohmic contacts were made on one face of the pellets with an In–Ga eutectic alloy, which gives the ohmic behavior. The whole pellet, except the front surface, was cemented with an epoxy resin to prevent any short-circuit between the electrical contact and the electrolyte.

Apparatus. Electrochemical measurements were made with a "three-electrode device": the active electrode described above, a platinum-counter electrode and a saturated calomel electrode (SCE). The electrolyte was a 1 *M* NaOH solution (pH

13.3). All the anode potentials are referred to the SCE.

Photocurrents were measured with a Tacussel PRT 20-2X potentiostat under the outputs of a 150-W Xe lamp and of a grating monochromator. The observed photocurrents were corrected for a spectral distribution of the light source and of the monochromator. The quantum efficiencies were determined by dividing the electron flow in the external circuit by the incident rate of photons passing through the monochromator and an uv cut-off filter for the visible light.

Mott-Schottky measurements to determine the flat-band potential of the electrode, were performed in the frequency range 10–30 kHz with a lock-in amplifier.

Results and Discussion

Influence of Mechanical Polishing

Four kinds of undoped $SrTiO_3$ electrodes corresponding to the different surface treatments, described above, were studied. All the samples had almost the same conductivity and gave very low dark currents even after the surface treatments ($i_{dc} < 10^{-6}$ A for $-1.0 < V < 0.3$ V). Their photocurrent-potential curves under illumination of polychromatic visible light ($\lambda > 400$ nm), are shown in Fig. 2. Mechanical polishing of the electrodes produces a large response in the visible region.

Table I compares the values at three different wavelengths and $V = 0$ V, of the quantum efficiency (η) for the untreated and polished polycristalline electrodes with that for the single-crystal $SrTiO_3$ electrodes studied by Butler *et al.* (*38*). It should be noted that, at 450 nm, the η values of the polished samples are 120 times larger than that of the untreated electrode.

Influence of Chemical Etching and Annealing

As shown in Fig. 2, the unpolished samples (O) and the polished and then etched samples (pol.-et.) exhibit a similar behavior.

The polished semiconductors reverted to their original characteristics after 5 min etching in concentrated nitric acid at 120°C. In fact it was found that the visible photoresponse decayed to zero as the etching time increased from 0 to 5 min. The weight loss measured after 5 min etching corresponded to a dissolution of about 0.5 μm of the thickness of the material from the surface. Wilson *et al.* also noticed that a depth

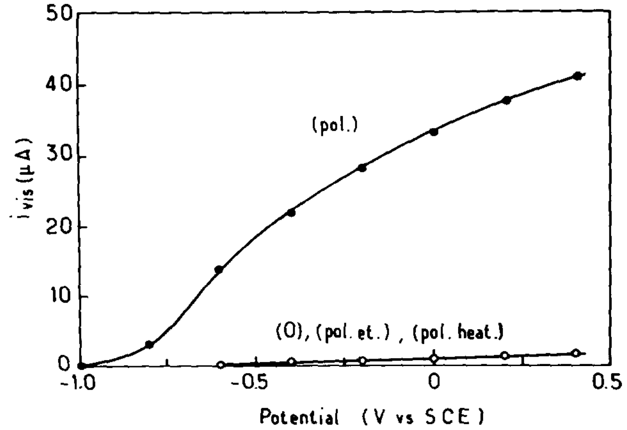


FIG. 2. Photocurrent-potential curves of the undoped $SrTiO_3$ electrodes in 1 *M* NaOH ($\lambda > 400$ nm).

TABLE I

QUANTUM EFFICIENCIES OF UNTREATED AND POLISHED POLYCRYSTALLINE ELECTRODES AND OF A $SrTiO_3$ SINGLE CRYSTAL ELECTRODE (V = 0 V)

Sample	Quantum efficiency (η)		
	400 nm	450 nm	500 nm
(0)-$SrTiO_3$	1.8×10^{-4}	1.5×10^{-5}	—
(pol.)-$SrTiO_3$	9.5×10^{-3}	1.9×10^{-3}	1.0×10^{-3}
Single crystal $SrTiO_3$ (38)	3×10^{-5}	2×10^{-5}	4×10^{-6}

of the order of 1 μm must be etched away to remove the effect of mechanical polishing in TiO_2 single-crystal electrodes (*49*). We can assert that the polishing treatment affects the whole depletion layer because its width is usually less than 0.5 μm.

The (pol.-heat.)-$SrTiO_3$ electrode also showed very weak response to visible light; thus the annealing treatment reverses the effect of polishing. This result indicates that the polishing treatment induces bond weakening (as it appears in an amorphous material) or surface defects that either disappear or are made benign (by reordering) with heating.

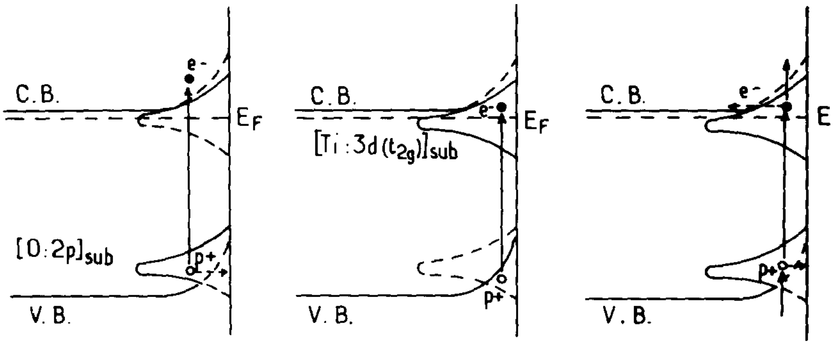
From the above results we may conclude that mechanical polishing of the electrodes introduces band-gap energy states associated with bond breaking, bond weakening, or other crystalline defects in a surface layer. Band-gap energy states in the depletion layer allow the production of a visible photocurrent. The density of these states, probably very large at the surface, decreases with distance from the surface; it becomes negligible at about 0.5 μm from the surface.

Possible Mechanisms

Bond weakening or surface defects tend to be eliminated by an anneal that provides the thermal energy required for restructuring. Broken bonds introduce electron states deep in the energy gap, whereas a reduced symmetry at the surface only introduces states near the band edge. Broken oxygen bonds associated with cation vacancies, introduce acceptor states $[O\colon 2p]_{sub}$ lifted out of the $O^{2-}\colon 2p^6$ valence band; broken cation bonds, as occurs at anion vacancies, introduce donor states, $[Ti\colon 3d(t_{2g})]_{sub}$, lowered out of the π^* conduction band of $Ti^{4+}\colon 3d(t_{2g})$ parentage.

As illustrated in Fig. 3, introduction of broken bonds can sensitize a large band-gap semiconductor to visible light by possible three absorption processes:

(i) The photocurrent may be due to direct excitation of electrons from the $[O\colon 2p]_{sub}$ states into the conduction band, followed by a tunneling of the photogenerated holes in the $[O\colon 2p]_{sub}$ levels into the valence band



(i) (ii) (iii)

FIG. 3. Possible processes giving rise to an anodic visible photoresponse.

in response to the depletion layer electric field.

(ii) Electrons may be photoexcited from the valence band to empty [Ti: $3d(t_{2g})]_{sub}$ levels from where they tunnel to the conduction band.

(iii) Excitations of electrons between the [O: $2p]_{sub}$ and [Ti: $3d(t_{2g})]_{sub}$ states, could be followed either by tunneling of carriers (electrons and holes) to the valence and conduction band or by additional photoexcitation.

Model

The double tunneling or double (or triple) excitation process (iii) can be reasonably neglected since it generally results in very small photocurrents (*38*).

In addition, if no electron-hole recombinations occur, the onset potential of the visible photocurrent can be correlated to an "effective" flat band potential (V'_{fb}). Under the assumptions that $\alpha w \ll 1$ and $\alpha L_p \ll 1$ the following correlation between the photocurrent i_p and the applied potential V can be obtained for process (i) (*51, 52*):

$$i_p^2 = (e\Phi_0 \alpha W_0)^2 (V - V'_{fb}) \qquad (1)$$

where e is the electronic charge, Φ_0 the incident photon flux, α the optical absorption coefficient, W_0 a constant depending upon the properties of the semiconductor (W is the depletion layer thickness) and L_p the minority-carrier diffusion length. A similar expression can be derived for process (ii).

Figure 4 shows i_p^2 vs V curves at 350 and 460 nm (i.e., above and below band-gap illumination) for the polished electrodes.

The curve for 350 nm presents a good linearity above -0.2 V; it extrapolates to -1.35 V at $i_{350}^2 = 0$. This value agrees quite well with the flat-band potential of a $SrTiO_3$ electrode. A $V'_{fb} \simeq V_{fb}$ is to be expected for above band-gap radiation.

The curve of Fig. 4 corresponding to the visible photocurrent of (pol.)-$SrTiO_3$, can be divided into two parts: in the potential range above -0.5 V it shows good linearity with an extrapolated value of $V'_{fb} \simeq -0.65$ V; and for $V < -0.5$ V, the square of the photocurrent decreases exponentially, as the potential becomes more negative. This curve might be extrapolated to V_{fb} at $i_{460}^2 = 0$, as observed by Butler *et al.* (*38*).

It follows, that processes (i) and/or (ii), predominate for $V > -0.5$ V. At more negative potentials, tunneling from acceptor or donor states to band states is improbable, because of inadequate band bending in the depletion layer. Thermal excitations among the donor or acceptor states are required for tunneling to the broad bands in the po-

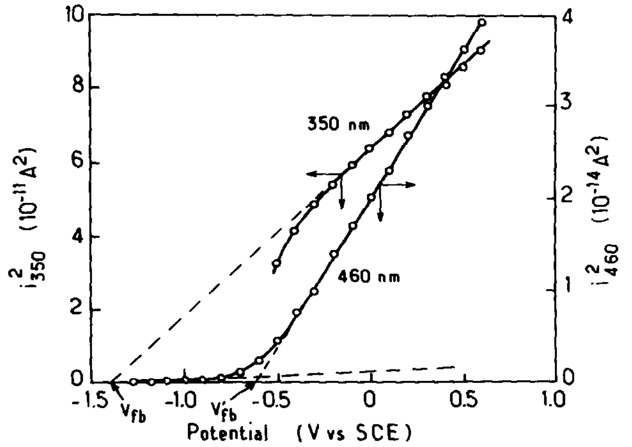


FIG. 4. Square of the photocurrent vs potential for (pol.)-$SrTiO_3$ anode in 1 *M* NaOH.

tential range $V_{fb} < V < V'_{fb}$. Deep traps associated with weakened or broken bonds thus appear to be located about 0.7 eV ($|V_{fb}| - |V'_{fb}|$) from the Fermi level, they probably lie in a narrow defect band ($|Ti: 3d(t_{2g})|_{sub}$).

In order to illustrate the influence of polishing on the quantum efficiency η of the anodes, the wavelength dependence of η at 0 V, is shown in Fig. 5. Polishing the sample results on a decrease of the uv photocurrent; the band-gap states introduced by polishing apparently act as intermediary centers for secondary recombination processes between the photogenerated conduction band electrons and valence-band holes. The decrease of the uv response is largely compensated by the remarkable increase of the visible photoresponse. Profile 2 is compatible with two absorption maxima, one about 1 eV wide at 500 nm and the other narrower and peaking at about 430 nm. Only the first would be accessible to 460-nm radiation.

Energy Diagram

Figure 6 is a schematic energy diagram at the flat band potential V_{fb} for a (pol.)–Sr TiO_3 electrode in 1 *M* NaOH. The potentials are referred to the saturated calomel electrode. The diagram is deduced from the above results and the following remarks:

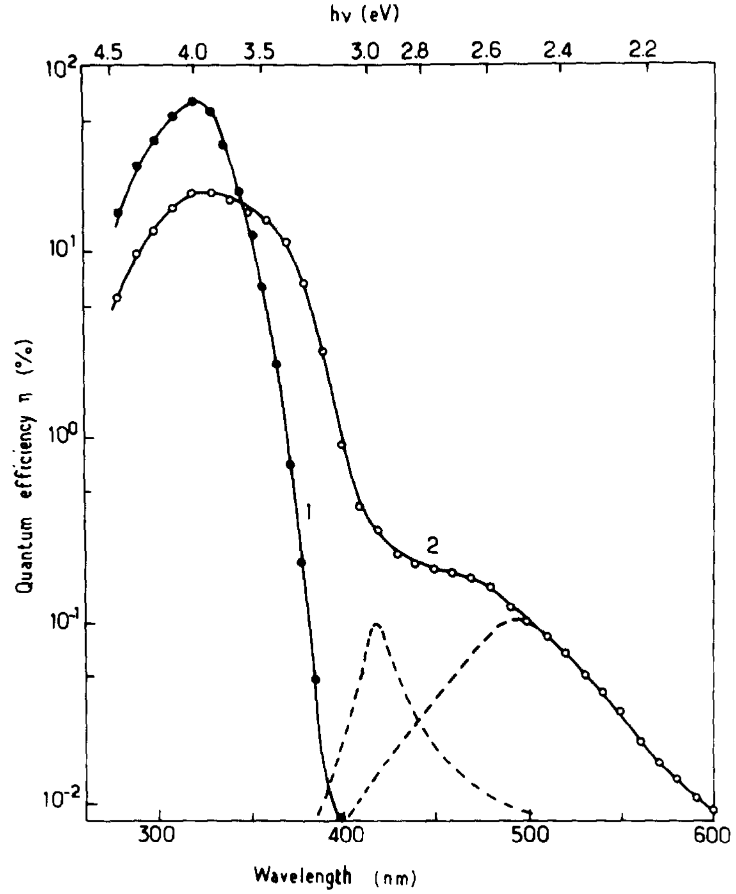


FIG. 5. Wavelength dependences of photocurrent for the untreated (1) and polished electrodes (2) (1 *M* NaOH; $V = 0$ V).

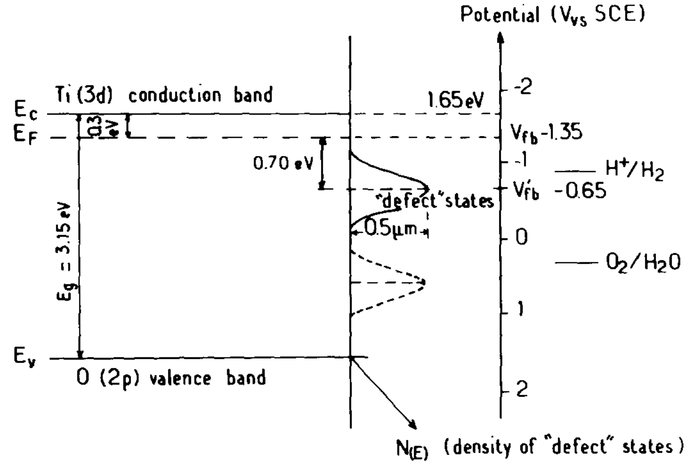


FIG. 6. Energy level diagram for polished and undoped $SrTiO_3$ electrode (1 *M* NaOH) at the flat-band potential.

(i) The energy gap $E_g = 3.15$ eV, deduced from $(\eta h\nu)^{1/2}$ vs $h\nu$ plots (obtained from Fig. 5), measures the splitting between the top of the valence band E_v and the bottom of the conduction band E_c.

(ii) Suitably doped n-type samples are characterized by $E_C - E_F \simeq 0.3$ eV and we assume this value to hold in our samples. As $V_{fb} = -1.35$ V E_C will be set at -1.65 V.

(iii) The defect band $|\mathrm{Ti}\colon 3d(t_{2g})|_{sub}$ is located at 0.7 eV below the Fermi level. This value corresponds to the voltage difference between the true flat band potential (V_{fb}, i.e., uv light) and the pseudo-flat band potential (V'_{fb}, i.e., visible light).

(iv) The density of the "defect" energy states (N_E) decreases with distance from the surface, becoming negligible at about 0.5 μm from the surface.

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