

Importance of the band gap energy and flat band potential for application of modified TiO₂ photoanodes in water photolysis

M. Radecka^{a,*}, M. Rekas^a, A. Trenczek-Zajac^a, K. Zakrzewska^b

^a Faculty of Material Science and Ceramics, AGH-University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland

^b Faculty of Electrical Engineering, Automatics, Computer Science and Electronics, AGH-University of Science and Technology, al. Mickiewicza 30, 30-059 Krakow, Poland

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Abstract

The influence on water photolysis of two important parameters of the electronic structure of photocatalytic semiconductors: the forbidden band gap, E_g , that decides about the absorption spectrum and the flat band potential, V_{FB} , that affects the recombination probability, was studied. The photoelectrochemical experiments were performed in a three-electrode cell PEC with a TiO₂ thin film photoanode immersed in liquid electrolyte of variable pH. Titanium dioxide photoanodes doped with chromium (up to 16 at.%) and tin (up to 50 at.%) were prepared by rf reactive sputtering. Different methods of flat band potential determination: Mott–Schottky plots and photocurrent versus voltage characteristics were used. The energy band gap was derived from the spectrophotometric measurements of optical transmittance and reflectance coefficients of thin films. For TiO₂ + 7.6 at.% Cr high and negative flat band potential $V_{FB} = -0.72$ eV (at pH 4) has been found but the recombination time $\tau = 8$ s was the shortest of all TiO₂ modifications. Despite additional absorption feature at about 2.8 eV, i.e., at wavelength corresponding to visible range of the light spectrum, the photoconversion efficiency of TiO₂ + 7.6 at.% Cr was found to be much smaller ($\eta_c = 0.1\%$) than that of undoped TiO₂ ($\eta_c = 1.8\%$) and TiO₂ doped with 8 at.% of Sn ($\eta_c = 1.0\%$).

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1. Introduction

Photoelectrochemical splitting of water is an environmentally friendly method of hydrogen generation based on renewable and apparently unlimited natural resources such as water and solar energy. Assisted by solar radiation, direct splitting of water into molecular hydrogen and oxygen was demonstrated for the first time in 1972 by Fujishima and Honda [1] in a photoelectrochemical cell PEC with an n-type semiconductor TiO₂ photoanode.

Since that time, many efforts have been undertaken to improve the conversion efficiency of the process but more than 30 years later this method is still far from commercialization. The reasons for this are fundamental and come as a consequence of a considerable mismatch between the spectra of light absorption in TiO₂ and that of solar radiation. Many other semiconductors such as GaAs had been tried as a replacement for wide-band-gap

TiO₂ (3.0 eV rutile, 3.2 eV anatase) before it was realized that severe requirements imposed on the photoanode material could not be met simultaneously by any existing semiconductor. These requirements include:

- (i) high stability and resistivity to corrosion and photocorrosion;
- (ii) low cost and availability;
- (iii) conduction band minimum, E_C , above the H₂O/H₂ electrochemical level of water reduction $E_C > E_{H_2O/H_2}$;
- (iv) valence band maximum E_V below the O₂/H₂O electrochemical level of water oxidation $E_V < E_{O_2/H_2O}$;
- (v) effective absorption of photons of the solar spectrum related to the band gap in the photon energy range of 1.6–1.9 eV.

As titanium dioxide in the form of anatase fulfils all but the last one condition, it has been admitted that the best way to the improvement of the performance of the photoelectrochemical devices would be to modify the absorption spectrum of TiO₂.

* Corresponding author. Tel.: +48 126172526; fax: +48 126172493.
E-mail address: radecka@agh.edu.pl (M. Radecka).

This can be achieved by shifting the fundamental absorption edge to longer wavelengths or by creating additional absorption features within the band gap. The methods tried up till now include: cation doping [2], sensitization with organic dyes [3], composite materials [4], and recently proposed, anion doping with N, C or S [5]. However, whereas it is relatively easy to affect the absorption spectra of TiO₂ by these methods, this is not in general true for the photocatalytic efficiency. The limiting factor is the recombination rate of the photoexcited electrons and holes.

Therefore, there are two important parameters of the electronic structure of photocatalytic semiconductors: the forbidden band gap that decides about the absorption spectrum and the flat band potential that affects the recombination probability. Fig. 1 explains the meaning of these parameters.

At the interface between the semiconducting photoanode and the electrolyte, the band bending occurs (see Fig. 1). It is a result of interface phenomena: solid-electrolyte. Moreover, the Fermi level E_F in a semiconductor and electrochemical level E_{redox} in the electrolyte are equal at the equilibrium state. The space charge region is formed at the interface. This space charge region provides a strong electric field that is indispensable for an effective separation of photoexcited electrons from holes. On the other hand, if light is absorbed in the bulk of the photoanode, the photoexcited electrons and holes are created but there is a high probability they will recombine before being used for water photolysis. Therefore, if light is absorbed in this region, charge separation and field-assisted transport are expected.

The band bending is also affected by the external voltage V_B . For a given semiconductor and electrolyte, there exists a unique potential for which the potential drop between the surface and the bulk is zero and there is no space charge layer. This is the flat band potential V_{Fb} . From the point of view of the

photoelectrochemical process it is desired to have the flat band potential large and negative.

In this work, we have used TiO₂ thin films as photoanodes in the process of water photolysis. Thin films were deposited by rf reactive sputtering and modified by cation dopants such as Cr and Sn.

It is well-established, especially in the case of TiO₂ thin films [6,7], that technological conditions of a deposition process affect the crystallographic structure, microstructure and surface properties. The substrate temperature during film growth, oxygen partial pressure and doping have a tremendous impact on the interplay between two polymorphic forms of TiO₂, i.e., anatase and rutile. A significant contribution from the amorphous phase dominates at lower growth temperatures [7]. It has been demonstrated [8] that the anatase is the best form of all titanium dioxide polymorphs as far as the photoactive properties are concerned.

In our previous papers [9,10] we have reported on the comprehensive structural and morphological studies of undoped and modified by cation doping TiO₂ thin films grown by sputtering. Here, we concentrate on the importance of the flat band potential and band gap energy (forbidden band gap) for application of these materials in the water photolysis. It should be pointed out that these parameters are very sensitive to the changes in the film microstructure and morphology.

The aim of this work is to show how different modifications of TiO₂ affect both the flat band potential and the forbidden band gap. The influence of these parameters of the electronic structure on the photoelectrochemical efficiency of water splitting will be demonstrated.

2. Experimental

2.1. Preparation of modified TiO₂ thin film photoanodes

Titanium dioxide thin films were deposited by sputtering of Ti target in Ar + O₂ reactive gas atmosphere onto different substrates such as Corning glass, amorphous silica, titanium and carbon foils, NaCl, etc., depending on the requirements imposed by further applications [9–14]. In the case of photoanodes, Ti foil was used as a substrate. Modification of TiO₂ properties was achieved by cation doping with Cr and Sn. Chromium-doped TiO₂ photoanodes were obtained by sputtering from mosaic Ti + Cr targets. It was possible to reach up to 16 at.% of Cr in TiO₂ thin films by changing the relative target area covered with Cr discs. Deposition of TiO₂–SnO₂ thin films required much higher degree of technical sophistication related to the target construction. This was a consequence of a large difference in the melting points of Ti (1940 K) and Sn (500 K) as well as in the sputtering rates of these two metals in the atmosphere containing oxygen. Photoanodes of TiO₂ containing up to 50 at.% of Sn were obtained by sputtering from a dielectric Ti/SnO₂ target of varied surface coverage with SnO₂.

The influence of a variety of technological parameters such as the substrate temperature T_S and oxygen partial pressure on the film properties has been investigated. Detailed description of rf and dc magnetron sputtering systems used for deposition of

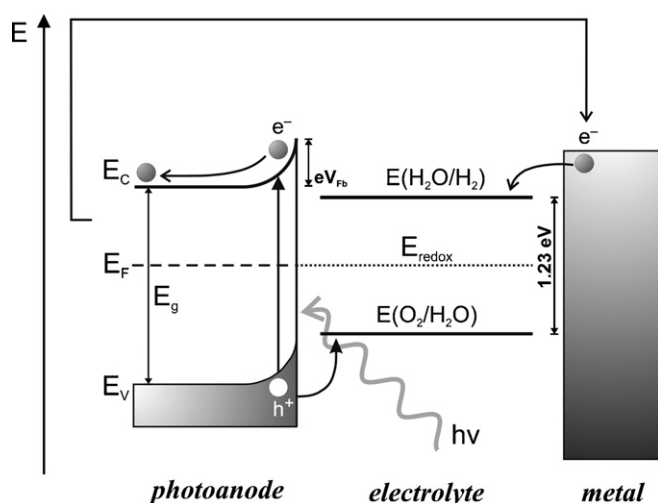


Fig. 1. Energy E diagram of the semiconducting photoanode/liquid electrolyte/metallic cathode system used for water photolysis. The flat band potential, V_{Fb} and band gap, E_g are shown. Energy levels separated by 1.23 eV and corresponding to redox reactions $E(\text{H}_2\text{O}/\text{H}_2)$, $E(\text{O}_2/\text{H}_2\text{O})$ as well as the conduction and valence band edges are included. Upon the absorption of photon of the energy $h\nu$ a pair of electron e^- and a hole h^+ is created.

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