DC sputter deposited TiO$_2$ layers on FTO: towards a maximum photoelectrochemical response of photoanodes

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ABSTRACT

In this work, we examine the photoelectrochemical response of TiO$_2$ layers prepared by reactive DC sputter deposition on conductive glass (FTO). We show that adequate conditioning of the FTO by a very thin (few nm thick) Ti interlayer and optimizing the sputter parameters, compact TiO$_2$ anatase layers can be produced that reach incident photocurrent conversion efficiencies (IPCE) maxima peaking at 75%. This is outperforming many of the best titania photoanode structures (including high surface area 1D and 3D titania structures). The key role of the interlayer is to promote the crystallization of titania in the anatase form during the annealing process (as opposed to rutile in the interlayer-free case). Without this interlayer, an IPCE maxima of \( \approx 43\% \) is obtained for otherwise identically processed electrodes. The present work thus describes a most simple straightforward approach for fabricating compact, high-efficiency TiO$_2$ (anatase) photoanodes.
Introduction

Over the past decades, titanium dioxide has attracted wide interest for its use in photocatalysis and photoelectrochemistry (PEC), particularly to produce self-cleaning devices, for pollution degradation, or as electron conductor in various types of solar cells [1]. A most widely investigated photocatalytic application is water splitting without or with an applied electrochemical potential (i.e., in a PEC system) to produce di-hydrogen from water. The key element of a PEC system is a semiconductor, where upon superband gap illumination, electron–hole pairs are generated on conduction and valence band, respectively. These charge carriers are then separated by the applied field and transferred to back contact and electrolyte, respectively. In a photoanode, electrons migrate to the back contact and holes react at the photoanode surface with the electrolyte in an oxidation reaction. Among various semiconductor materials for photoanodes, TiO$_2$—the classic photocatalyst—still attracts wide attention due to its nearly unrivaled set of properties (especially a very high photocorrosion stability) [2, 3]. Back-contacted titania layers have been produced over the years by many different techniques. Frequently investigated electrodes were back contacted single crystals, anodic layers, and most commonly layers deposited on transparent electrodes—typical examples are layers produced by doctor blading or spray pyrolysis on transparent conducting glass (such as FTO) [4–8].

In more recent years, 1D or 3D geometries, such as tubes, wires, rods, flakes, etc. of TiO$_2$ have become extensively investigated [3, 9–21]. Compared to bulk or compact TiO$_2$ layers, electrodes made of 3D assemblies of nanostructured TiO$_2$ are widely considered more effective electrodes as they provide a higher surface area, a higher number of reaction sites, and the nanoscale geometries may allow for orthogonal (beneficial) electron/hole separation [22]. In photoelectrochemical investigations, these advantages of 3D morphologies have been extensively reported to provide a significantly higher solar-to-electricity conversion efficiencies than obtained for compact films [22]. This is frequently expressed quantities by the incident photon-to-current conversion efficiency (IPCE) [23–25] that may typically range from 5–60% for differently produced titania samples. Among different factors, the IPCE for titania photoanode depends strongly on the crystal structure of TiO$_2$. Titanium dioxide is typically found in the crystalline forms of rutile, anatase or brookite. In general, the anatase polymorph (in spite of a higher band gap of $\approx 3.2$ vs. $E_g \approx 3.0$ eV of rutile) is the best photoanode, due to a better electron mobility and conductivity. In view of the electrode geometry, typical IPCE data (acquired under moderate anodic bias and in the UV range) are 5–20% for compact films [9, 21, 26]. For 3D structures, typical IPCE values are reported as 15–35% for nanotubes [9–11, 21], 40–65% for nanoflakes [18, 27], 15–30% for nanowires [1, 22], and 2–8% for compacted nanoparticle photoanodes [9, 29, 30]. The better IPCE performance for
the 3D structures often is ascribed to the higher surface area of the corresponding geometries. Nevertheless, in this simple explanation, it is often overlooked that for anatase considerable photocurrent recombination via surface states has been reported [31]. In other words, in view of this recombination reaction, an enhancement of the surface area is detrimental and the benefit (larger charge carrier exchange area) versus the drawback (much higher number of surface states) should be properly evaluated. Here, we address exactly this point by examining different factors that may optimize compact anatase TiO$_2$ layers on FTO—this then allows a re-assessment of literature reports on the relative efficiency of different (anatase) photoanode geometries.

Over the years, different approaches have been developed for the production of compact TiO$_2$ thin layers, such as wet chemical deposition methods (spin-coating, spray coating, dip-coating), chemical vapor deposition (CVD) and physical vapor deposition (PVD) (thermal evaporation, ion/electron beam evaporation and reactive sputtering) [32]. Among them, the reactive magnetron sputtering technique notably stands out for its defined features, a high packing density and a great deal of control over the intrinsic material properties, and the production of precise and uniform thickness layers [16, 17, 32]. Depending on the exact deposition parameters, layers of anatase, rutile or mixed phase crystal structures have been reported. The crystallinity and particularly the crystal phase of the sputtered titania layers is significantly influenced by the basic sputtering conditions such as total pressure, oxygen partial pressure, substrate negative bias, substrate temperature and discharge current [33–35].

In spite of numerous investigations [36], systematic investigations of sputter parameters and the resulting performance of titania photoanodes seem to be scarce. In the present work, we therefore investigate DC-sputtered anatase TiO$_2$ layers in view of their annealing and their back contacting on the performance of photoanodes, with the goal to achieve a maximum IPCE.

Most notably, we introduce a conditioning approach of the FTO with a thin metallic Ti layer before titania sputtering that yields reliably to full anatase layers. For such layers, we find IPCE values of up to 75.8% in aqueous electrolytes (without any hole capture agent)—these are values that are similar or even superior to most advanced 3D nanostructured photoanodes.

**Experimental**

**FTO substrate preparation**

TiO$_2$ compact layers were fabricated on fluorine-doped tin oxide (FTO, 7 $\Omega$/sq., Pilkington) by reactive DC magnetron sputtering (DC-MS). The FTO substrates were preliminarily cleaned by sonication in acetone, ethanol and deionized (DI) water in sequence for 15 min each, and then dried in a N$_2$ stream. Subsequently, they were mounted in a load-lock (LL), whose pressure was then reduced until equal to that of the main sputter chamber (SC, Createc—SP-P-US-6 M-3Z). The cleaned substrates were afterwards transferred to the SC ready for the sputtering process.

**Ti target cleaning**

Prior to film deposition on FTO, a target (Ti, 5”, 99.995%, dia. 127 mm x 8 mm, HMW—Hauner GmbH & Co. KG) cleaning process was implemented under pure Ar to eliminate the passivating oxide layer mainly due to previous sputtering. Firstly, the base pressure ($P_b$) was adjusted to 1.5 $\times$ 10$^{-7}$ mbar and the turbo-molecular pump speed reduced from 100 to 20%. With the low pump speed, Ar gas (4 sccm) was then introduced into the SC. As the working pressure ($P_w$) reached and stabilized at 1.4 $\times$ 10$^{-3}$ mbar, DC power was applied from 50 to 500 W for 10 min with a closed shutter for the purpose of target cleaning.

**Deposition of TiO$_2$ and TiO$_2$/Ti layers**

TiO$_2$ layers were deposited by reactive DC-MS method with the cleaned Ti target in SC. Ar gas (10 sccm) and O$_2$ gas (5 sccm) were filled into the SC until $P_w$ stabilized at 6.7 $\times$ 10$^{-3}$ mbar. Oxygen partial pressure was set as 33.3%. The gases were precisely controlled by mass flow controllers (MFC, MKS Instruments, Inc.) and the distance between the target and the substrates was kept at 115 mm. Reactive sputtering was carried out at room temperature and with a circulating cooling water system for magnetron cooling. To grow uniformly thick TiO$_2$ layers
on top, the sputtering process was performed at 500 W for an optimized time, with the substrate holder rotating at 20 rpm.

For TiO$_2$/Ti samples, a thin layer of Ti metal was deposited with the same target prior to TiO$_2$ compact oxide layer deposition. The substrate holder was firstly set to rotate (50 rpm) for uniform deposition. Subsequently, 150 W of DC power was applied for 10 s to accomplish the deposition of a Ti interlayer on a FTO glass.

The deposited layers on FTO were then annealed, in a tubular furnace, at different temperatures for 1 h in air.

**Characterization**

The surface morphology and cross-sections of the prepared TiO$_2$ layers were studied by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

The crystal structure of the TiO$_2$ layers was identified by X-ray diffraction (XRD, X’pert Philips MPD with a Panalytical X’celerator detector) using graphite monochromatized Cu K$_\alpha$ radiation (wavelength 1.5406 Å). The approximate size of TiO$_2$ crystallites was calculated by the Scherrer equation [28, 37, 38].

For IPCE of the TiO$_2$ layers, transient photocurrent response was recorded under chopped light illumination for each sample. The photocurrent measurements were performed in a 3-electrode cell comprising a TiO$_2$ sample as a working electrode, Pt foil as a counter electrode, and an Ag/AgCl reference electrode. As an electrolyte an air-saturated solution of 0.1 M Na$_2$SO$_4$ in either pure DI water was used. During the measurements a potential of 0.5 V (vs. Ag/AgCl) was constantly applied to the working electrode.

IPCE spectra in the wavelength range of 300–600 nm were recorded using an Oriel 6365 150 W Xe-lamp as a light source. From the broad emission spectrum of the lamp, monochromatic radiation at specific wavelengths was produced by an Oriel Cornerstone 7400 1/8 m monochromator.

Voltage dependent photocurrent data were recorded in the range of −1 to 1 V (vs. Ag/AgCl) with potential steps of 100 mV at a constant wavelength of 325 nm using a Jaissle IMP 88 PC potentiostat.

**Results and discussion**

Figure 1a–c shows SEM images of a typical TiO$_2$ layer sputtered on a SiO$_2$ or an FTO substrate under mixed gas conditions ($P_{O_2} = 33\%$) for 4 h. This sputter time results in a thickness of the TiO$_2$ layers on FTO and SiO$_2$ of approx. 200 nm. Then, a set of samples was prepared using different oxide sputter times to systematically vary the sample thickness. All layers are relatively flat with some structural features that become increasingly defined with oxide thickness. The SEM images in Fig. 1d show cross-sections of layers on FTO for different sputter times. Thickness variations from $\approx 50$ to $\approx 400$ nm were established by the different sputtering times from 1 to 8 h, respectively. As evident from Fig. 1d, with an increase in sputter time, a reasonably linear increase in film thickness is obtained.

After annealing all the layers in air at 450 °C for 1 h, XRD diffraction patterns were acquired as shown in Fig. 1e. For the thinnest layer of $\approx 50$ nm thickness only a very weak diffraction signal corresponding to TiO$_2$ crystalline phases could be detected (so, average crystallite size is calculated as 7.8 nm). For the thicker layers, clearly the presence of anatase phase was evident. The average crystallite size estimated from the diffraction peaks using the Scherrer equation was 17.2–21.3 nm (as expected slightly increasing with increasing sputter-time).

IPCE spectra for the series of samples in Fig. 1f were then measured in 0.1 M Na$_2$SO$_4$. From the spectra, it is clear that the magnitude of the photocurrent maximum (at approx. 320 nm) increases with the layer thickness from IPCE $\approx 30\%$ for the 50 nm thick layers to $\approx 75\%$ for the 200 nm thick layers. I.e., for these layers the observed increase in IPCE can be ascribed to an increasing total light absorption. For the sample of an even higher thickness of 400 nm, however, a drop in the IPCE magnitude occurs. This decrease at thicknesses $> 200$ nm may be due to an increasing transport path of charge carriers to the back contact. This transport path length is even more increased for shorter wavelength as the absorption coefficient in the deep UV is even higher. These aspects on IPCE maximum and absorption length are explained in previous work in more detail [9].

The spectra in Fig. 1g can be replotted to evaluate the indirect band gap ($E_g$) of the titania layers. Such an evaluation for an indirect band-gap yields for all
samples with >50 nm thickness $E_g = 3.2$ eV. This value is well in line with literature data reported for anatase. Evidently, in the case of the 50 nm thick oxide film, the determination of the optical band-gap yields $E_g \approx 3.0$ eV which fits in fact to rutile [39].

Please note that the XRD peaks in Fig. 1e are very weak and do not allow for an unambiguous assessment of the crystalline form of this sample.

Most importantly, please note that an IPCE maximum of $\approx 75\%$ for the 200 nm thick anatase layer is in
the order of 3 times higher than commonly reported for compact titania layers and is in the same range of the best 3D structures.

In a next set of experiments, we kept the thickness of the sputtered layer constant at the optimized value of 200 nm and annealed the layers at different temperatures from 250 to 800 °C.

Figure 2a shows XRD diffraction spectra for the layers treated at different annealing temperatures. For all annealing temperatures from 250 to 800 °C, clear peaks of anatase (and tin oxide) can be seen. The crystallinity increased with increasing temperature up to 450 °C, as visible also from the average crystal size. From the Scherrer equation we obtain average crystallite size 18.6–21.2 nm (in general increasing with the annealing temperature). Importantly, for annealing temperature of 700 °C and higher, tin oxide peaks become clearly apparent because Sn of the FTO glass starts diffusing at a significant rate into the TiO₂ layer [40].

Figure 2b shows IPCE spectra for the samples annealed at different temperatures. The magnitude of the IPCE increases with increasing annealing temperature up to 550 °C; however, for 700 °C and higher, the magnitude of photocurrents drops significantly. In view of the XRD results, evidently the doping of the TiO₂ with Sn species is detrimental for the efficiency of the photoanode. Please note that for the sputtered layers and higher annealing conditions, we do not observe a conversion of the anatase films to rutile—in the literature this conversion is often given as a reason for a decay of photoanodes annealed a T > 700 °C—based on our results this must however rather be ascribed to detrimental Sn-doping.

Figure 2c show a re-plot of the IPCE spectra for the evaluation of the band-gaps of the titania films. Evidently, for all our layers we obtain 3.2 eV, i.e., the typical band-gap of anatase (fully consistent with the XRD data). As mentioned, all data of this work were obtained using a Ti-interlayer (of a few nm thickness) sputtered on the FTO prior to reactive sputtering for...
the oxide layers. The use of this interlayer was based on some preliminary experiments in our lab regarding the conditioning FTO [41]. Without this thin interlayer, drastically different results are obtained. Not only the crystallinity of the layers after annealing are affected but also the IPCE is significantly reduced. This is illustrated in Fig. 3a and b. Figure 3a shows XRD data for 200 nm thick titania layers that were sputtered on FTO without the Ti-interlayer. In contrast to the data in Fig. 2a, the layer annealed at 550 °C contains significant amounts of rutile and the layer annealed at 800 °C is entirely converted to rutile. (If the layers are sputtered using the thin metallic interlayer, the oxide consists in both cases entirely of anatase (see Fig. 2a)). Figure 3b shows photocurrent spectra for the layers sputtered without the interlayer. The IPCE that can be obtained from the Ti-interlayer-free TiO₂ sample after annealing at 550 °C is only 43% instead of 75% (with the interlayer). For the sample annealed at 800 °C, the IPCE drops from ≈30 to 23% without the interlayer. For both annealing temperatures (without the interlayer), the band-gap results as E₉ ≈ 3.0 eV which corresponds to rutile instead of anatase.

Overall, it is clear that a main effect of the interlayer is that it leads to preferential anatase crystallization of the titania layers during the annealing process.

Finally, we examined the effect of the applied voltage on the photocurrent of the TiO₂ layers of a different thickness. Figure 4 shows I_ph at different voltages measured at a fixed light wavelength of 350 nm. Clearly, all layers show a behavior that is roughly in line with I_ph ∝ (U - U_fb)⁰.₅ [24, 25]. If the data is replotted according to I_ph² vs. U (Fig. 4, inset), the straight lines provide U_fb of ≈ -0.2 V. This is well in line with data provided in the literature for flat band data of TiO₂ in a neutral electrolyte [10, 42]. Evidently, the limiting photocurrent magnitude is provided by the layer thickness up to ≈200 nm. I.e., in this thickness range of layers the maximum photocurrent is limited by the physical thickness of the sputtered TiO₂ layer rather than the depth of the space charge layer.
Overall, the most remarkable point of the present work is that the work shows that it is possible by optimizing the sputtering and annealing conditions to fabricate compact TiO$_2$ (anatase) layers that are as efficient as photoanodes as most effective mesoporous layers or 1D or 3D structures used in literature as photoelectrodes. In other words, the present work shows that gain in surface area for anatase electrodes is not key to maximize the photocurrent. The reason for this is likely that for anatase surfaces recombination losses seriously limit the maximum photocurrent [31].

From the present work, it seems that the main practical limitation for compact layers is the quality of the anatase layers (phase purity and crystallinity) produced by reactive sputtering on FTO. Clearly, the use of a thin Ti interlayer drastically aids to overcome this drawback and this enables compact photoanodes of a quality similar to 3D electrodes.

**Conclusions**

In this work, we examine the photoresponse of TiO$_2$ photoanodes prepared by reactive DC sputter deposition on conductive glass (FTO).
The results presented in this work show that by optimizing the sputter parameters as well as the annealing treatment of the compact sputtered TiO₂ layers, incident IPCE values of 75% can be reached—this is comparable to the best 3D structures reported. This maximum efficiency is obtained for 200 nm thick anatase layers after annealing at 450–550 °C in air. For higher annealing temperatures, we find detrimental incorporation of Sn into anatase.

We also point out the importance of using a very thin (few nm thick) Ti interlayer on the FTO before depositing the oxide species by reactive sputtering. The interlayer promotes the crystallization of anatase in the annealing process (as opposed to rutile in the interlayer-free case). Or most directly, without the interlayer an IPCE of only 43% instead of 75% is obtained for otherwise identically processed electrodes.

Most remarkable is that an IPCE value of 75% is in the range of highest achieved photocurrent conversion efficiencies using 1D or 3D structures (such as nanowires, nanotubes, etc.). This shows the high potential for such sputter deposited layers fabricated under optimized conditions.

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