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Electrochemical characterization of TiO₂ blocking layers prepared by reactive DC magnetron sputtering

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Abstract

Thin TiO₂ (anatase) films were prepared by reactive DC magnetron sputtering and characterized in detail. Specifically, they were tested as compact blocking underlayers in dye-sensitized solar cells. Elastic recoil detection analysis and optical measurement showed some porosity in the sputtered films, but electrochemical measurements demonstrated good blocking characteristics. This suggests the presence of small voids rather than pinholes in the deposited films. In the case of an iodide/iodine redox couple, thin underlayers (~20 nm) improved the fill factor without affecting other properties of

the cell. In case of a ferrocene / ferrocenium-based electrolyte, the presence of underlayers was necessary to obtain functional dye-sensitized solar cells.

Keywords: Thin solid films; dye-sensitized solar cells; redox mediators.

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Introduction

Dye-sensitised solar cells (DSCs) based on mesoporous TiO_2 have attracted much attention due to their promise for low-cost photovoltaics [1-3]. It has been found that improvements in the solar cell efficiency can be achieved in these devices when a thin, compact blocking layer of TiO_2 is deposited on the conducting substrate before deposition of the mesoporous film. In the most common version of the DSC, that uses fluorine-doped tin oxide (FTO)-coated glass as the substrate and a liquid redox electrolyte containing the triiodide / iodide redox couple, the TiO_2 blocking layer reduces the recombination of electrons in the FTO and triiodide in the electrolyte [4-7]. The positive effect of the TiO_2 blocking layer is rather small as the reduction of triiodide is already rather slow on bare FTO electrodes. When other redox couples are used, however, such as Co-complexes [8, 9] and ferrocene / ferrocenium [10], and when solid hole conductors, such as spiro-MeOTAD [2, 11], CuSCN [12] and CuI [13] are used instead of an I^-/I_3^- electrolyte, the presence of a blocking layer is essential to obtain a functioning DSC.

Besides TiO_2 , other materials have been investigated as blocking layers, namely insulating polymers [10], Nb_2O_5 [14, 15], MgO , ZnO , Al_2O_3 , Eu_2O_3 and SiO_2 [15]. The majority of investigations deal, however, with TiO_2 blocking layers prepared by various methods. Spray pyrolysis is most commonly used, [4-7, 11] but also sol-gel techniques, screen-printing [16], radio frequency magnetron sputtering of Ti followed by oxidation [17] and reactive sputtering of TiO_2 [18-20] have been applied.

In earlier work we have used reactive sputtering to obtain porous nanocrystalline TiO₂ electrodes that were successfully applied in DSCs [21, 22]. By carefully changing the deposition parameters, we were able to obtain dense TiO₂ anatase films. Here we report on the characterization of the latter films and on their performance as blocking layers in DSCs using I⁻/I₃⁻ and ferrocene / ferrocenium as redox mediators. Very thin sputtered TiO₂ layers (~20 nm) appear to be most suited for application as blocking layer in DSCs.

Experimental

The titanium oxide films were deposited onto microscope glass slides (Menzel GmbH) and fluorine-doped tin oxide (FTO)-coated glass substrates (TEC 8, 8 Ω/square, Hartford Glass Company, Inc. USA). The substrates were first cleaned using a detergent, rinsed in deionized water and dried in a stream of nitrogen gas, and then sonicated for 10 min in warm (55°C) acetone (>99.0 %), rinsed in deionized water and dried using nitrogen. Thin TiO₂ films were deposited by reactive DC magnetron sputtering using a Balzers UTT 400 system with a titanium target (5 cm diameter, purity 99.9 %). A constant DC current of ~550 mA and a power of ~ 240 W were applied. After pumping down to ~10⁻⁷ mbar, argon gas (99.998%) was introduced into the sputtering chamber. To remove surface contaminants on the target, pre-sputtering was done for ~10 minutes in pure argon. Oxygen (99.998%) was then introduced into the chamber. The O₂/Ar ratio was maintained at 0.07 while the working pressure was ~7 mTorr. Substrates were positioned ~ 13 cm from the target, rotated during deposition and kept at a temperature of 330 ± 10° C. Temperatures of the frontside of the glass substrates were calibrated in separate runs,

which was necessary since the thickness was different for the microscope slides and the FTO-coated glass. The deposition rate was $\sim 4.2 \text{ nm min}^{-1}$.

Film thicknesses were determined using a Tencor Alpha-step 200 surface profilometer equipped with a diamond stylus. For very thin layers, the thickness was inferred by means of extrapolation of the relation between film thickness and deposition time obtained for thicker samples. A Siemens D5000 diffractometer was used for X-ray diffraction (XRD). The stoichiometry of the films was estimated from Elastic Recoil Detection Analysis (ERDA) using the time of flight technique with iodine ions at 40 MeV and a recoil angle of 45° . Optical transmittance and reflectance were measured in the wavelength range 0.3 to $2.5 \mu\text{m}$ by a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrating sphere. A plate of barium sulphate was used as reference for the reflectance measurements.

Electrochemical characterization was performed using a CH Instruments 660A potentiostat. TiO_2 -coated FTO working electrodes were sandwiched with thermally platized FTO counter electrodes [23] using a frame of thermoplastic (Surlyn 1702). An electrolyte composed of 0.6 M tetrabutylammonium iodide, 0.1 M LiI, 0.1 M I_2 and 0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile, was introduced through a hole in the counter electrode that was sealed with Surlyn and cover glass afterwards. In some experiments a ferrocene / ferrocenium (Fc/Fc^+) redox electrolyte was used. This electrolyte was prepared by adding the oxidizing agent nitrosonium tetrafluoroborate to a

solution containing 0.10 M Fc and 0.1 M LiCF₃SO₃ in 3-metoxypionitrile to obtain a final concentration of 0.09 M Fc and 0.01 M Fc⁺.

Dye-sensitized solar cells were prepared using standard methods. Briefly, a colloidal TiO₂ paste was applied onto the electrodes using doctor blading followed by heating in a hot air flow at 450°C for 30 minutes, thus forming a mesoporous TiO₂ layer of ~8 µm thickness. After cooling to 80°C, the electrodes were immersed in an ethanol solution of N719 dye overnight. After rinsing and drying, the sensitized electrodes were assembled with a counter electrode and filled with electrolyte as stated above. Current – voltage (IV) curves under 1000 W/m² AM 1.5 G illumination were measured using a Newport solar simulator (Model 91160) and a Keithley 2400 source/meter.

Results and discussion

X-ray diffraction spectra of the sputtered TiO₂ films on conducting glass substrates are shown in Figure 1. Besides strong SnO₂ peaks from the substrate, peaks from crystalline TiO₂ [24] are visible. In very thin films (~20 nm) only one TiO₂ peak is found: anatase (004), suggesting preferential crystal growth along this direction. From the peak broadening a crystal size of 19 nm is calculated using the Scherrer equation. In films thicker than 100 nm other anatase peaks (A(101) and A(200)) appear, as well as some weak rutile peaks (R(101) and R(111)). The predominant phase is anatase also for the films deposited on plain glass.

ERDA measurements were carried out for films on plain glass. The stoichiometry was found to be TiO_x with $x=1.96\pm0.03$ and porosities of about 0.1 to 0.25 were inferred. A more clear dependence of the porosity on film thickness was obtained from analysis of optical measurements of films deposited on plain glass slides. The refractive index and the extinction coefficient were computed from experimental reflectance and transmittance data by a formalism based on Fresnel's equations for a thin film on a substrate [25]. The porosity, P , of the films was estimated using the relation [26]

$$P = 1 - \frac{(n_m^2 + 2)(n_f^2 - 1)}{(n_m^2 - 1)(n_f^2 + 2)} \quad (1)$$

where n_m and n_f are the refractive indices of bulk anatase TiO_2 and the sputtered film, respectively. The refractive index of bulk anatase TiO_2 is 2.46 (average in the wavelength range 500-2500 nm) [27]. Figure 2 shows the refractive index for the films, averaged over the wavelength region where the extinction coefficient was not significantly different from zero, i.e 500 -2500 nm, and the corresponding porosity according to eq. (1), as function of film thickness. It is seen that the refractive index exhibits a pronounced maximum for film thicknesses of about 100 to 150 nm, which corresponds to a minimum in porosity. The porosity, as obtained from optical and ERDA data, exhibits values of the same order of magnitude. Compact films with porosities of the order of 0.1 or lower can be reproducibly obtained.

The current – voltage characteristics of sputtered TiO_2 films on FTO were recorded in an electrolyte containing the iodide / triiodide redox couple. Typical results in the negative

potential range, where the current is due to reduction of triiodide according to $I_3^- + 2 e^- = 3 I^-$, are shown in Figure 3. The presence of a sputtered TiO_2 film decreases the current significantly as compared to the bare FTO substrate at potentials in the range of 0 to -0.5 V. At more negative potentials the difference in current becomes less, and at about -0.7 V the currents are equal. Additional annealing of the sputtered films at 450 °C for 30 min. in air did not have a significant effect. It has been shown that TiO_2 films prepared by spray pyrolysis show a similar blocking behavior [4, 5]. The observed potential-dependent blocking behavior can be explained by the presence of band bending in the TiO_2 film. The concentration of electrons at the TiO_2 /electrolyte interface increases therefore as the potential becomes more negative.

The blocking behavior of the sputtered TiO_2 films was further analyzed using ac-impedance spectroscopy. Figure 4a shows impedance data of a sputtered TiO_2 /(I_3^- / I^-) electrolyte system in a Nyquist plot recorded at different applied potentials. The impedance data is well fitted using the equivalent circuit shown in Figure 4b, consisting of a series resistance and two parallel resistor – capacitor (RC) circuits. The semicircle in Fig. 4a at lower frequencies corresponds to the RC circuit from the TiO_2 -coated FTO electrode, while at higher frequencies a much smaller semicircle is present (not visible in Fig. 4a, because the charge transfer resistance at the counter electrode is about 3 orders of magnitude smaller than that of the TiO_2 -coated FTO electrode). In contrast to findings in the study of Cameron and Peter [4], no evidence for electrolyte-induced surface states was found. The charge transfer resistance of the TiO_2 electrode is shown in Figure 4b as a function of film thickness. It is evident that the TiO_2 coating increases the charge-transfer

resistance, by about one order of magnitude. The film thickness (18 -210 nm) does not appear to play a signification role, indicating that the thinnest films are already sufficiently pinhole free. Additional annealing of the sputtered films does not have a significant effect. The impedance results agree well with the voltammetry results. The electrochemical results suggest that the porosity observed in the sputtered TiO₂ films does not give rise to pinholes. There are, however, probably small isolated voids in the film.

Dye-sensitized solar cells prepared using sputtered blocking layers were tested. Typical current –voltage curves are shown in Figure 5. Very thin blocking layers (~20 nm) improved the IV characteristics of the solar cells. More specifically, the fill factor was improved by ~5%. A similar effect has been reported for DSCs with spray-coated TiO₂ underlayers [6]. This effect can be directly related to the decrease in recombination losses of electrons to the electrolyte at the FTO substrate. Blocking layers being 50 nm and thicker, however, decreased the fill factor and thereby the overall solar cell efficiency. Variations in the photocurrent were attributed to differences in the quality and thickness of the porous TiO₂ films that were manually deposited on top of the blocking layers using the doctor blading technique. Further analysis of the IV curves suggests that thicker blocking layers add an additional series resistance to the solar cells, thereby decreasing the fill factor.

The decay of the open circuit potential of a solar cell in darkness, after a period of illumination, is a useful and easy method to investigate recombination processes in solar

cells [28]. The voltage decay was significantly slower when a sputtered TiO₂ underlayer was present in the solar cells, indicating that a significant part of the recombination between electrons in the working electrode and triiodide in the electrolyte occurs via the FTO substrate in the absence of the TiO₂ underlayer. Similar results have been observed before for spray-coated TiO₂ underlayers [4]. The initial voltage decay (around -0.7 V) is, however, not significantly affected. This is in agreement with the linear sweep voltammetry measurements (Figure 3) that show that the blocking behavior of the sputtered TiO₂ underlayers is only apparent at potentials lower than -0.7 V. From the voltage decay transients ($V(t)$) electron lifetimes in the TiO₂ can be calculated using $\tau_e = -kT/e (dV/dt)^{-1}$, where k is Boltzmann's constant, e is the electron charge and T is temperature [28]. The inset in Figure 6 shows that the sputtered underlayers improved τ_e by a factor ~ 2 in the voltage range of -0.6 to -0.3 V.

Additional measurements using small modulations of the incident light were performed. The open-circuit photovoltage response of the solar cells to the modulated light yielded lifetimes that were consistent with the results obtained with the voltage decay mentioned above. Short-circuit photocurrent response demonstrated that the TiO₂ underlayer did not affect the electron transport time significantly (data not shown).

Finally, dye-sensitized solar cells with sputtered TiO₂ underlayers were tested using a fast one-electron redox couple: ferrocene / ferrocenium (Fc/Fc⁺). Current – voltage characteristics in the dark and upon illumination are shown in Figure 7. At overpotentials less than 100 mV, the anodic and cathodic dark currents were decreased by the sputtered

blocking layer by ~ 2 orders of magnitude compared to solar cells without underlayers on the FTO. Currents were, however, ~ 2 orders of magnitude larger than in the case of the iodide / triiodide electrolyte, because of the much faster kinetics of the ferrocene-based redox couple. The thickness of the blocking layers (18 – 320 nm) did not have a significant effect on the measured dark currents (data not shown).

Under illumination, relatively small short circuit photocurrents ($\sim 0.1 \text{ mA cm}^{-2}$) and open-circuit photovoltages ($\sim 0.15 \text{ V}$) were found for solar cells with underlayers, while there was no significant photovoltaic effect in the solar cells where the porous TiO_2 layer was deposited on the bare FTO; see Figure 7b. Interestingly, there appeared to be an approximately linear relation between the blocking layer thickness and the photocurrent, see inset in Figure 7b. As the blocking behavior was not much affected by the sputtered layer thickness, we ascribe this effect to the increase in roughness of the compact layers with thickness. It appears that mainly dyes attached on the underlayer contribute to the photocurrent. Electrons injected from dyes adsorbed at the porous TiO_2 film seem to recombine with ferrocenium ions during transport to the substrate, as they are in close contact with the electrolyte. Electrons injected from dyes adsorbed at the TiO_2 blocking layer, on the other hand, can reach the FTO without encountering the electrolyte. On a perfectly flat TiO_2 surface, about $10^{-10} \text{ mol cm}^{-2}$ of N719 can be absorbed, assuming that these molecules occupy 1.65 nm^2 each [3]. Ideally, the light absorbed by this monolayer should give a photocurrent of $34 \text{ } \mu\text{A cm}^{-2}$ under one sun illumination. Thus, a roughness factor of ~ 3 is sufficient to account for the observed photocurrents. It should be noted that

excitation of TiO_2 by the UV part of the solar light might also account for some of the photocurrent.

Conclusions

TiO_2 blocking underlayers prepared by reactive sputtering can be obtained with low porosity. The good blocking behavior of these films suggests that the porosity can be attributed to small isolated voids. Sputtered blocking layers have a small and subtle effect in dye-sensitized solar cells with the iodide/iodine redox couple, where thin layers (~ 20 nm) appear to improve the fill factor without affecting other properties of the cell. In case of the Fc/Fc^+ electrolyte functional DSCs could only be formed in cells with TiO_2 underlayers.

Acknowledgements

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Figure captions

Figure 1. X-ray diffraction spectra of sputtered TiO₂ films on FTO glass substrates.

Figure 2. Average refractive index (a) and porosity calculated from eq. (1) (b) as a function of film thickness. The refractive index was averaged over the wavelength range 500-2500 nm.

Figure 3. Linear sweep voltammograms of TiO₂ blocking layers on FTO glass substrates in I⁻/I₃⁻ electrolyte (0.6 M tetrabutylammonium iodide, 0.1 M LiI, 0.1 M I₂ and 0.5 M 4-tert-butylpyridine in 3-methoxypropionitrile). The TiO₂ film thickness is indicated. Sandwich cells with electrode area of 0.48 cm² were prepared using a FTO + TiO₂ working electrode and a platinized FTO counter electrode. Scan rate 10 mV s⁻¹.

Figure 4. Electrochemical impedance spectroscopy of TiO₂ blocking layers on FTO glass substrates in I⁻/I₃⁻ electrolyte. Data were recorded by use of the same cells as in Fig. 3. (a) Nyquist plot of a cell with a 112 nm thick TiO₂ blocking layer at 3 applied potentials. 12 frequencies were measured per decade; the lowest frequency shown is 0.21 Hz. (b) Charge-transfer resistance of FTO electrodes coated with sputtered TiO₂ films of different thickness. The electrodes were polarized at -0.5 V vs. the counter electrode. Filled circles indicate samples that had received an additional annealing step in air at 450 °C. The equivalent circuit used to fit the ac-impedance data is shown. The charge transfer resistances at the electrodes are denoted R_{ct} .

Figure 5. IV characteristics of dye-sensitized solar cells with compact TiO₂ underlayers in simulated sunlight (1000 W m⁻², AM1.5G). Porous TiO₂ films (~8 μm thick) were deposited on top of the sputtered underlayers. An I⁻/I₃⁻ electrolyte was used.

Figure 6. Open-circuit voltage decay transients of dye-sensitized solar cells with compact TiO₂ underlayers. Inset shows the calculated lifetimes vs. voltage.

Figure 7. IV characteristics of dye-sensitized solar cells with and without compact TiO₂ underlayers in ferrocene / ferrocenium electrolyte in darkness (a), and under illumination (1000 W m⁻², AM1.5G), (b). The inset in (b) shows the short-circuit photocurrent as function of TiO₂ underlayer thickness. Porous TiO₂ films (~2 μm thick) were deposited on top of the sputtered underlayers.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7