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Postprint

This is the accepted version of a paper published in *Solar Energy Materials and Solar Cells*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the original published paper (version of record):

Sorar, I., Pehlivan, E., Niklasson, G., Granqvist, C. (2013)
Electrochromism of DC magnetron sputtered TiO₂ thin films: Role of deposition parameters.
Solar Energy Materials and Solar Cells, 115: 172-180
<http://dx.doi.org/10.1016/j.solmat.2013.03.035>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-204258>

Electrochromism of DC magnetron sputtered TiO₂ thin films:

Role of deposition parameters

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Abstract

We performed a comprehensive study on the electrochromism in TiO₂ thin films made by reactive DC magnetron sputtering and elucidated the roles of sputter gas pressure p , O₂/Ar gas ratio γ and substrate temperature τ_s . Good mid-luminous optical modulation—taken to be ~50 % in ~200-nm-thick films—was obtained under charge exchange in a Li⁺ electrolyte for $p > 15$ mTorr and $\tau_s < 100$ °C, whereas γ was less important. The deposition rate dropped for increasing p , and hence $p \approx 15$ mTorr was optimal. These films were X-ray amorphous and contained some water. The coloration efficiency η was ~25 cm²/C, which exceeds data on η in most prior studies on sputter deposited TiO₂ and verifies that such films can display the same values of η as those of TiO₂ films made by several chemical techniques.

Keywords: Electrochromism; Thin films; Titanium dioxide; Sputter deposition; Deposition parameters

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1. Introduction

Electrochromic (EC) materials are able to change their optical properties reversibly and persistently by charge insertion/extraction [1,2]. They can be integrated in multilayer constructions devised for energy efficient windows, information displays, etc [3]. EC-based fenestration is of much current interest and can provide significant energy savings in buildings [4–8] jointly with a comfortable indoor climate [9,10].

A conventional EC device incorporates a tungsten oxide thin film separated from another thin film serving as a counter electrode by an ion conductor, and this three-layer stack is embedded between transparent electrical conductors for inserting/extracting the charge [1]. Tungsten oxide colors under charge insertion, i.e., cathodically. Ideally, the counter electrode should color under charge extraction, i.e., anodically, and a hydrous nickel oxide film is a particularly good option for devices [11–13]. Another alternative is to have an essentially non-coloring counter electrode.

Thin films and nanoparticles of TiO_2 can display EC properties, and this material has attracted sporadic interest for almost forty years. However, the observed optical properties have not been consistent among different studies, and TiO_2 has been suggested to serve as a cathodically coloring material as well as an essentially non-coloring one; prior literature is surveyed in Sec. 2 below. Having thus set the scene, we turn to a detailed study on the electrochromism in thin TiO_2 films made by reactive DC magnetron sputtering, which is a technique particularly well suited for large-area, large-scale manufacturing [3,14]. Section 3 describes thin film deposition by reactive DC magnetron sputtering as well as materials characterization, and Sec. 4 reports how the EC properties depend critically on, in particular, the pressure and oxygen/argon mixing ratio in the sputter plasma and on the temperature of the substrate onto which the deposition takes place. Conclusions are given in Sec. 5. We find that proper choices of deposition parameters lead to films with EC coloration efficiencies on a par with those for the best TiO_2 films prepared by several alternative techniques and reported in earlier literature.

2. Literature review

A thorough examination of the scientific literature has identified numerous previous studies on the electrochromism of TiO_2 -based thin films and particle coatings. Table I

summarizes the most important of these studies and reports film preparation technique and EC efficiency for charge insertion/extraction. The latter property is expressed in terms of a coloration efficiency η taken to be the difference in optical density per amount of charge insertion/extraction. Except when otherwise noted, the data pertain to Li^+ exchange. In general η depends on the wavelength λ , but for our purposes it is sufficient to state a value that is typical for the luminous range, i.e., for a value in the $400 < \lambda < 700$ nm interval.

We first consider some films made by evaporation [15,16], whose coloration efficiency was found to be small. Specifically, Seike and Nagai observed $\eta \approx 5 \text{ cm}^2/\text{C}$ [15].

Sputter deposition has attracted more widespread interest, and TiO_2 -based films have been prepared by RF [17–23] and DC techniques [24–27]. A number of studies have reported small values of η [17–19,21–23,27] and results from most of them are not included in Table I. However, we note early work by Cogan et al. [17] who observed $\eta \approx 5 \text{ cm}^2/\text{C}$ across the luminous wavelength range. Significantly larger values were subsequently found by Kitao et al. [20], who reported $\eta \approx 9 \text{ cm}^2/\text{C}$ for Li^+ exchange and $\eta \approx 14 \text{ cm}^2/\text{C}$ for H^+ exchange. An apparently simultaneous study by Yoshimura et al. [26] shed light on the reason why η may vary among different investigations and demonstrated that the coloration efficiency could go from a low value up to as much as $\eta \approx 29 \text{ cm}^2/\text{C}$ when the pressure of the sputtering gas was increased and its composition was varied. These results are important as a motivation for our present investigation and point at the critical role of the film nanostructure and that in general deposition parameters promoting porosity lead to large coloration efficiency. A similar result, though less detailed, was found in work by Lee [22]. An investigation of sputter deposited titanium oxyfluoride films by Azens et al. [24,25] yielded a record value of η as large $37 \text{ cm}^2/\text{C}$; this was interpreted as a consequence of fluorine incorporation leading to a highly porous, yet electrochemically stable, structure of the thin films. Quenching of the electrochromism, which may be of interest for optically passive electrodes in EC devices, can be accomplished by adding CeO_2 to the TiO_2 [28,29].

Sol-gel deposition has been employed in numerous investigations [30–40]. The early works by Dœuff and Sanchez [30] and by Özer et al. [33,34] were particularly important and proved for the first time that large values of η could be accomplished for TiO_2 -based films made by any technique. Other studies have given the coloration efficiencies indicated in Table I, with maximum values of $33 \text{ cm}^2/\text{C}$ for H^+ exchange in the work by Gillet et al. [31,32] and $29 \text{ cm}^2/\text{C}$ for Li^+ exchange in the work by Ivanova and Harizanova [38]. The latter study, as well as the one of Wang and Hu [35], are of special significance and demonstrated a range of

coloration efficiencies depending on heat treatment temperature and that η dropped as the films became denser upon annealing at high temperatures.

Chemical bath deposition has been used several times to make TiO_2 -based films with EC properties [41–44] and have yielded the coloration efficiencies shown in Table I. A value as high as $\eta \approx 26 \text{ cm}^2/\text{C}$ was reported by Richardson and Rubin [41]. The studies by Lin et al. [42] and Wang et al. [43] indicate again that annealing and accompanying densification tend to decrease the coloration efficiency.

Among electrochemical methods for making TiO_2 -based films we note that anodization [45] as well as cathodic electrodeposition [46] have been used. The very recent work by Lee et al. [45] showed $\eta \approx 16 \text{ cm}^2/\text{C}$ when the anodization conditions were appropriate for making a “mesoporous” structure. Anodization can be used also for preparing nanotubes, and such samples have shown electrochromism both in H^+ [47–49] and Li^+ electrolytes [50–53]. It seems that these latter samples are less porous than the mentioned “mesoporous” one, and their coloration efficiencies are not as high.

There are other techniques that are applicable too. Thus a doctor blade technique has been employed recently by Dinh et al. [54,55] and has given TiO_2 films with $\eta \approx 34 \text{ cm}^2/\text{C}$. Furthermore, studies have been conducted on films made by chemical vapor deposition [56,57].

For completeness we also observe that a large amount of work has been performed on samples comprising particles and, in fact, the original discovery of an EC effect in TiO_2 was reported in 1974 when color changes of oxide particles in a resin binder had been detected upon polarization between transparent conducting substrates [58]. Subsequent studies have shown reversible color changes, of possible interest for display devices, in TiO_2 powder compacts prepared in various ways [59–65]. Such compacts have also been used as nanoporous substrates for efficient adsorption of molecular redox chromophores (especially viologens)—in much the same way as for dye sensitized solar cells [66]—which has led to materials of relevance for high-quality reflective EC displays [67–88]. Powder compacts comprised of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were investigated recently and yielded pronounced electrochromism [89] (which may be inferred also from some prior battery-related work [90,91]). Furthermore, electrochromism has been observed in porous titania glass [92].

Finally we note that reversible switching between brightly colored titanium-based surfaces can be accomplished electrochemically by increasing and decreasing an AC voltage

in a stepwise manner [93]. This unusual phenomenon appears to be caused by concurrent thin film growth and dissolution and hence is not “electrochromic” in the sense we define the term.

3. Experimental

3.1 Sputter deposition

Thin films of TiO_2 were prepared by reactive DC magnetron sputtering onto glass substrates pre-coated with $\text{In}_2\text{O}_3\text{:Sn}$ (indium tin oxide, denoted ITO) having a sheet resistance of $15 \, \Omega/\text{square}$. Depositions were performed in a versatile system based on a Balzers UTT 400 unit. The chamber was evacuated to $\sim 10^{-7}$ Torr, and argon and oxygen (both of 99.998 % purity) were then admitted through mass-flow-controlled inlets. Sputtering took place from a 5-cm-diameter metallic titanium target (99.995 % pure) at a constant current of 0.75 A. The target–substrate separation was 13 cm. Pre-sputtering was conducted for 5 minutes in pure argon, and oxygen was then introduced at a constant rate in order to make TiO_2 films. Each of the depositions was carried out under constant conditions confined to the following parameter space:

- pressure p of the sputter plasma in the range $10 \leq p \leq 40$ mTorr,
- oxygen/argon ratio γ of $1.7 \leq \gamma \leq 4$ %, and
- substrate temperature τ_s of $25 \leq \tau_s \leq 300$ °C.

The substrates were rotated during the depositions to ensure even coatings. The investigation included 28 samples in total.

Deposition rate r was inferred from the thickness of a film, removed from the deposition chamber, and its corresponding deposition time. Figure 1 shows rates for a number of samples prepared under different magnitudes of p and γ and for $\tau_s \approx 25$ °C. It is seen that r drops monotonically from ~ 20 to ~ 5 nm/minute as p is increased from 10 to 40 mTorr, and that the dependence on γ is weak. The tendency of increased oxygen contents giving lower deposition rates is associated with “substrate poisoning”—i.e., the formation of poorly conducting titanium oxide on the target—and similar results have been documented repeatedly in prior work (for example in Refs. [94,95]).

3.2 Film characterization

Film thicknesses were recorded with a Bruker Dektak XT surface profilometer. Thicknesses were measured at four or more places of the samples and individual results were averaged. The samples were found to be 200 ± 20 nm in thickness.

Crystal structures of the TiO_2 thin films were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer operating with CuK_α radiation at a wavelength of 1.54 Å and with a grazing incidence angle of one degree for diffraction angles 2θ between 20 and 60 degrees. Figure 2 reports XRD data for TiO_2 films deposited with $p = 15$ mTorr, $\gamma = 4$ % and $100 \leq \tau_s \leq 300$ °C as well as for a bare ITO-coated glass plate. Nothing but diffraction lines due to ITO can be seen for $\tau_s < 150$ °C, and these TiO_2 films consequently are amorphous. Crystallinity sets in at $\tau_s > 150$ °C and then the diffraction peaks are consistent with the tetragonal anatase phase of TiO_2 , as is most evident for the (101) reflections at $2\theta \approx 25.4$ degrees (JCDPS Card No. 84-1286). Analogous results have been presented elsewhere (for example in Ref. [96]). The crystallite size was ~ 17 nm, as inferred from the Scherrer equation [97].

Film characterization by infrared (IR) spectroscopy in the $500\text{--}4000$ cm^{-1} range was performed on a Bruker Tensor 27 Fourier Transform (FT) instrument. The resolution was set to 4 cm^{-1} , and each spectrum was averaged over 100 scans. Figure 3 shows data for TiO_2 films deposited with $p = 15$ mTorr, $\gamma = 4$ % and $100 \leq \tau_s \leq 300$ °C as well as for a bare ITO-coated glass plate, i.e., for the same kinds of samples as those reported on in Fig. 2. All spectra display a broad minimum below 1000 cm^{-1} , which is consistent with Ti–O stretch modes in TiO_2 [98]. Furthermore there is a wide and shallow minimum between 3600 and 2800 cm^{-1} for the film deposited at $\tau_s \approx 25$ °C which is associated O–H stretch modes in loosely bound water [98].

Spectral normal transmittance $T(\lambda)$ and reflectance $R(\lambda)$ were measured in the wavelength range $300 \leq \lambda \leq 2500$ nm by use of a Perkin-Elmer Lambda 900 spectrophotometer equipped with a barium-sulfate-coated integrating sphere. A Spectralon plate served as reflectance standard. Figure 4 shows $T(\lambda)$ and $R(\lambda)$ for TiO_2 films deposited onto ITO; upper panel refers to $10 \leq p \leq 40$ mTorr, $\gamma = 4$ %, $\tau_s = 25$ °C and lower panel to $p = 15$ mTorr, $\gamma = 4$ %, $25 \leq \tau_s \leq 300$ °C. All films are transparent in the luminous wavelength range and reflect in the IR mainly as a consequence of the ITO. The drop of $T(\lambda)$ for $\lambda < 400$ nm ensues from absorption in TiO_2 [99] as well as in ITO and the glass substrate. Oscillations in the data are caused by optical interference; the patterns are rather similar for the various films in the two panels, which points at film thicknesses being almost equal.

Electrochemical measurements were carried out by use of a Solartron 1286 electrochemical interface and a standard three-electrode cell where TiO₂/ITO served as working electrode and Li as reference and counter electrodes. The electrolyte was 1 M LiClO₄ dissolved in propylene carbonate. Cyclic voltammetry (CV) measurements were executed at a scan rate 20 mV/s, and the potential was swept between 1 and 3.2 V vs Li/Li⁺. Transmittance changes of TiO₂/ITO films due to the charge insertion/extraction were measured *in situ* at $\lambda = 550$ nm on an Ocean Optics spectrophotometer; the 100%-level was taken as the transmittance of the cell containing nothing but electrolyte. All electrochemical measurements were performed under argon atmosphere in a glove box.

4. Electrochromism

Comprehensive measurements on CV, insertion/extraction of charge density (ΔQ), and optical modulation between bleached (*b*) and colored (*c*) states at $\lambda = 550$ nm (ΔT) were performed on films prepared under conditions represented by $10 \leq p \leq 40$ mTorr, $1.7 \leq \gamma \leq 4$ % and $25 \leq \tau_s \leq 300$ °C. Quantitative data on coloration efficiency were obtained from

$$\eta = \ln(T_b/T_c) / \Delta Q \quad (1)$$

The electrochemical reaction for ion exchange is expected to be [1]

with e^- denoting electrons.

4.1 The roles of sputter gas pressure and composition

We first consider TiO₂ films prepared on unheated substrates. Figure 5 reports results for the 10th CV cycle pertaining to TiO₂ films deposited at several different sputter gas pressures and with $\gamma \approx 4$ %. Most samples reached good electrochemical reversibility already after three to four cycles. The first scan began at 3.2 V vs Li/Li⁺ with films in their bleached states. The data for $p > 10$ mTorr show a consistent pattern with the cathodic current rising distinctly at ~ 2.3 V vs Li/Li⁺ and the anodic current having a broad maximum at ~ 1.7 V vs Li/Li⁺. Data for $p = 10$ mTorr look distinctly different from the other ones, and a cathodic peak stands out at 1.23 V vs Li/Li⁺.

The CV recordings allow evaluations of charge densities corresponding to ion exchange, and such data are shown in Fig. 6 for $10 \leq p \leq 40$ mTorr, $1.7 \leq \gamma \leq 4$ % and $\tau_s \approx 25$ °C. The lowest oxygen/argon mixing ratio yields a small charge density of ~ 12 mC/cm². The charge density rises with increasing value of p —which is consistent with the larger areas of the CV scans in Fig. 5—and reaches 32 ± 6 mC/cm² for $p > 15$ mTorr. The data do not permit any conclusion regarding an influence of the O₂/Ar content in the sputter gas.

Time-dependent optical transmittance at $\lambda = 550$ nm was recorded during the first ten CV scans for TiO₂ films deposited at $10 \leq p \leq 40$ mTorr, $\gamma = 4$ % and $\tau_s \approx 25$ °C. As shown in Fig. 7, there was some evolution of the optical data concurrently with the changes in the CVs and a trend that the bleached-state transmittance diminished slightly during the initial cycling. Samples prepared with $p > 10$ mTorr display a consistent pattern with a large optical modulation; samples made at $p = 10$ mTorr are different and the optical modulation is much smaller.

Figure 8 reports optical modulation after ten CV cycles for TiO₂ films prepared with $10 \leq p \leq 40$ mTorr, $1.7 \leq \gamma \leq 4$ % and $\tau_s \approx 25$ °C. It is seen that $p = 10$ mTorr yields $\Delta T = 17 \pm 3$ % whereas $p > 15$ mTorr leads to much superior values being $\Delta T = 48 \pm 7$ % with no apparent dependence on the O₂/Ar gas flow ratio. There is a striking resemblance between the optical modulation data in Fig. 8 and the charge exchange data in Fig. 6.

Coloration efficiency was extracted from data on charge insertion/extraction during ion exchange and optical data according to Eq. 1. Such data are reported in Fig. 9 for TiO₂ films prepared with $10 \leq p \leq 40$ mTorr, $1.7 \leq \gamma \leq 4$ % and $\tau_s \approx 25$ °C. The most interesting results are those for $p > 15$ mTorr, because only those films allowed large charge insertion/extraction and optical modulation. It is seen that $\eta = 24 \pm 2$ cm²/C pertains to those samples.

4.2 The role of substrate temperature

A complementary study, devised to investigate the role of substrate temperature, was performed on TiO₂ films prepared under conditions represented by $p = 15$ mTorr, $\gamma = 4$ % and $25 \leq \tau_s \leq 300$ °C. Figure 10 illustrates CV data from which one infers that results for $\tau_s \approx 25$ °C agree well with those at $p > 10$ mTorr in Fig. 5. The CVs for $\tau_s > 100$ °C are qualitatively different, though, and display anodic peaks at 2.3 V vs Li/Li⁺ and cathodic peaks at ~ 1.6 V vs Li/Li⁺. The CVs for $\tau_s = 100$ °C are intermediate. Figure 11 reports corresponding data on charge density, which is seen to drop from 30 mC/cm² for $\tau_s \approx 25$ °C, to 17 mC/cm² at $\tau_s \approx$

100 °C, and to stabilize at a value as low as $\sim 8 \text{ mC/cm}^2$ for $\tau_s > 100 \text{ °C}$; the former of these values agrees excellently with data in Fig. 6.

Time-dependent optical transmittance at $\lambda = 550 \text{ nm}$ was measured during the first ten CV scans for TiO_2 films deposited at $p = 15 \text{ mTorr}$, $\gamma = 4 \%$ and $25 \leq \tau_s \leq 300 \text{ °C}$. Figure 12 shows that the optical modulation is large for films made at $\tau_s \approx 25 \text{ °C}$, small for films prepared at $\tau_s > 100 \text{ °C}$, and intermediate when $\tau_s = 100 \text{ °C}$. Figure 13 displays corresponding results for coloration efficiency. The most interesting results are those for low values of τ_s , and then $\eta \approx 25 \text{ cm}^2/\text{C}$ is obtained, i.e., one recovers the result found in the study reported on in Sec. 4.1 above.

4.3 Cycling durability: Preliminary results

TiO_2 films were deposited onto ITO at $p = 25 \text{ mTorr}$, $\gamma = 4 \%$ and $\tau_s \approx 25 \text{ °C}$ and were cycled electrochemically as described in Sec. 3.2 for up to 10,000 times. Figure 14 shows CV data indicating that the current density drops monotonically as the cycling progresses. The data are in general agreement with CVs reported in Figs. 5 and 10. The charge density, which was 35.2 mC/cm^2 for the first cycle, dropped to 11.0 mC/cm^2 after 1000 cycles and further to 5.7 mC/cm^2 after 10,000 cycles. Corresponding coloration efficiencies lay in the interval $21 < \eta < 33 \text{ cm}^2/\text{C}$. The drop in current density may be due to irreversible Li exchange, chemical dissolution of the TiO_2 , or to a combination of these effects; it was not subjected to a detailed examination.

5. Conclusion

We carried out a comprehensive study on electrochromism in TiO_2 films prepared by reactive DC magnetron sputtering and elucidated the roles of the deposition parameters, specifically the sputter gas pressure, the O_2/Ar ratio and the substrate temperature. Good optical modulation—taken to be a 50%-interval for $\sim 200\text{-nm}$ -thick films—was obtained under charge insertion/extraction in a Li^+ -containing electrolyte when the substrate temperature during thin film deposition was low (below 100 °C , say) and the gas pressure in the sputter plasma was high enough (above $\sim 15 \text{ mTorr}$). For practical reasons, the thin film deposition rate must not be too small and one therefore concludes that a sputter gas pressure of $\sim 15 \text{ mTorr}$ may be optimal. These films were amorphous, as seen by X-ray diffraction, and showed traces of adsorbed water as revealed by infrared spectroscopy. The relationship

between sputter parameters and thin film structure is in overall agreement with literature data [100].

The fact that high sputter gas pressure and low substrate temperature were beneficial for electrochromic TiO₂ films is consistent with previous experience gathered from several different oxide films [101] and can be reconciled with “zone diagrams” for thin film evolution under various deposition conditions, such as the well known “Thornton diagram” [102] or one of its more recent elaborations [103–106]. These diagrams show that the deposition parameters mentioned above are expected to yield nanoporous films with pore axes perpendicular to the film surface. Such structures obviously are conducive to ion diffusion across the electrochromic films and hence to electrochromism.

We found the coloration efficiency of TiO₂ films with well developed electrochromism to be approximately 25 cm²/C. This is higher than for films made by sputtering and investigated in prior work, excepting the study by Yoshimura et al. [26]. This study gave results in full agreement with those in our work, albeit at a higher deposition pressure namely 60 mTorr. In particular, the work by Yoshimura et al. [26] pointed at the importance of conducting the sputtering at unusually high pressures (that are known to promote nanocrystallinity [107], analogously to the case of gas evaporation [108]). Furthermore, our observed coloration efficiencies are consistent with those in some studies on films prepared by sol-gel deposition [38], chemical bath deposition [41,43], and doctor blade technique [54,55]. Our earlier work on sputter deposition in the presence of CF₄ in order to make titanium oxyfluoride films is yet the one that produced the highest coloration efficiency (cf. Table I), but industrial-scale sputter deposition with fluorine-containing gases is more cumbersome (though not impossible [109]) than reactive deposition in argon and oxygen, which is extremely well proven in the vacuum coatings business [110].

Acknowledgement: IS’s work in Sweden was supported by a grant from the Scientific and Technological Research Council of Turkey (TÜBİTAK).

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Table I. Data for TiO₂-based thin films prepared by several techniques and having the shown values of coloration efficiency η for Li⁺ exchange (a few data for H⁺ exchange are indicated).

Preparation technique	η for Li ⁺ [cm ² /C]	Reference
Evaporation	~5	[15]
Sputtering (RF)	~5	[17]
	9 (Li ⁺), 14 (H ⁺)	[20]
Sputtering (DC)	37 (for oxyfluoride)	[24, 25]
	4–29	[26]
Sol-gel	14–33 (H ⁺)	[31, 32]
	10–20	[35]
	15	[37]
	9–29	[38]
Chemical bath deposition	26	[41]
	8	[42]
	< 25	[43]
	13	[44]
Anodization	16	[45]
Doctor blade technique	34	[54, 55]

Figure captions

Fig. 1. Deposition rate for TiO₂ films made by sputter deposition at the shown values of sputter gas pressure, O₂/Ar ratio (γ) and substrate temperature (τ_s). Data points were joined by straight lines for convenience.

Fig. 2. X-ray diffractograms of TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s). Peaks are assigned to the anatase (A) phase of TiO₂, as indicated by the dotted vertical lines. Bottom curve refers to uncoated ITO. The diffractograms are displaced vertically.

Fig. 3. FT-IR spectra of TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s). Upper dashed curve refers to uncoated ITO.

Fig. 4. Spectral transmittance and reflectance of TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s). Dashed curves refer to uncoated ITO.

Fig. 5. Cyclic voltammograms measured on TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s) and immersed in 1 M LiClO₄ dissolved in propylene carbonate. The voltage scan rate was 20 mV/s.

Fig. 6. Charge densities measured on TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure, O₂/Ar ratio (γ) and substrate temperature (τ_s). The data are based on cyclic voltammograms such as those shown in Fig. 5. Data points were joined by straight lines for convenience.

Fig. 7. Time-dependent optical transmittance at $\lambda = 550$ nm for TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s).

Fig. 8. Optical transmittance modulation at $\lambda = 550$ nm for TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure, O₂/Ar ratio (γ) and substrate temperature (τ_s). Data points were joined by straight lines for convenience.

Fig. 9. Coloration efficiency at $\lambda = 550$ nm for TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure, O₂/Ar ratio (γ) and substrate temperature (τ_s). Data points were joined by straight lines for convenience.

Fig. 10. Cyclic voltammograms measured on TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s) and immersed in 1 M LiClO₄ dissolved in propylene carbonate. The voltage scan rate was 20 mV/s.

Fig. 11. Charge densities measured on TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature. The data are based on voltammograms such as those shown in Fig. 10. Data points were joined by straight lines for convenience

Fig. 12. Time-dependent optical transmittance at $\lambda = 550$ nm for TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s).

Fig. 13. Coloration efficiency at $\lambda = 550$ nm for TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar (γ) ratio and substrate temperature. Data points were joined by straight lines for convenience.

Fig. 14. Cyclic voltammograms measured on TiO₂ films sputter deposited onto ITO at the shown values of sputter gas pressure (p), O₂/Ar ratio (γ) and substrate temperature (τ_s) and immersed in 1 M LiClO₄ dissolved in propylene carbonate. The voltage scan rate was 20 mV/s. Data are shown after the indicated numbers of cycles.

Figure 1

Figure 2

Figure 3

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Figure 12

Figure 13

Figure 14