

Anodization of Ti Thin Film Deposited on ITO

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We have investigated several key aspects for the self-organization of nanotubes in RF sputtered titanium (Ti) thin films formed by the anodization process in fluoride-ion-containing neutral electrolytes. Ti films were deposited on indium tin oxide (ITO) glass substrates at room temperature and 300 °C, and then anodized. The films were studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV–vis spectrometry before and after anodization. It was observed that anodization of high temperature deposited films resulted in nanotube type structures with diameters in the range of 10–45 nm for an applied voltage of 5–20 V. In addition, the anatase form of TiO₂ is formed during the anodization process which is also confirmed using photocurrent measurements. However, the anodization of room temperature deposited Ti films resulted in irregular pores or holes.

Introduction

Titanium dioxide (TiO₂) is one of the most studied metal oxides, which finds many applications in photocatalysis,^{1,2} dye-sensitized solar cells,^{3–5} self-cleaning,⁶ electrochemical devices,⁷ batteries,⁸ gas sensors,^{9–12} displays¹³ and photochromic devices,^{14–19} wettability applications,^{20,21} and so forth. Nanostructured forms of TiO₂ are currently under intense investigation, as they provide highly active surfaces with a large surface to volume ratio and unique properties. Physical and chemical manipulations in nanodimensions can be applied to enhance/alter the performance

of TiO₂ when it is used in the fabrication of micro/nanosize devices for commercial applications.

There are many routes for the production of TiO₂ nanoforms, of which, one of the most promising routes, even for commercial processes, is anodization. In this method, Ti, in the form of a film or foil, is anodized in fluoride-ion-containing electrolytes to form nanopores/tubes. For foils, it has been reported that, by controlling the anodization voltage and time, the nanotube/pore dimensions and aspect ratio can be varied to obtain a diameter of about 10–150 nm and a length of up to several hundreds of microns.^{22–31} Recently, Paulose et al.³² were able to increase the nanotube length up to 1 mm after the complete anodization of a 1 mm thick Ti foil film sample. They reported that achieving long nanotube arrays not only requires long anodization duration but also requires increasing concentrations of NH₄F and H₂O in the optimum electrolyte composition range.

Initially, Zwilling et al.^{33,34} demonstrated the possibility of forming self-organized, nanotubular surfaces of titanium oxide by anodic oxidation of a Ti foil. The Grimes and Schmuki groups have since conducted comprehensive studies on Ti foil anod-

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ization.^{24,28,35–44} However, the use of foil limits their potential applications, particularly in the fabrication of microscale devices, where thin films need to be deposited and patterned. Several research groups have developed alternative methods for the fabrication of nanoporous TiO₂ via the anodization of titanium films.^{45–50} One of the earliest studies was conducted by Mor et al.^{47,51} who used electrolyte containing acetic acid and hydrofluoric acid for the anodization of sputtered Ti films. They achieved 20–30 nm diameter nanotube arrays on RF sputtered deposited films at 500 °C using a variety of substrates including glass, silicon, and alumina. Anodization of thin films is a much less well-known process than foils due to its specific complications. The type of substrate is an important factor in the morphological formation and lattice orientation of Ti films. In addition, the deposition temperature, the stress mismatch of the substrate and Ti films, the thickness of the films, and the type of deposition all affect the films which in return affect the anodization process.

Different types of fluoride-ion-containing electrolytes such as acidic,³⁶ neutral,⁴⁶ aqueous, or nonaqueous electrolytes^{52,53} can be used in the anodization process. Grimes et al.²⁶ first showed that well-ordered arrays of nanotubes with high surface to volume ratio can be obtained using fluoride-ion-containing neutral nonaqueous electrolytes such as ethylene glycol. The use of ethylene glycol solvent may increase the nanotube growth rate to over 10 μm/h.²⁷ Additionally, nanotubes formed in ethylene glycol are nearly hexagonal and closely packed.^{26,54,55} There are many other methods for the manipulation of nanotubes such as the usage of multistep anodization⁵⁶ or altering the water content in the electrolyte.⁵⁷

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In this work, we have investigated the formation of nanotubes into RF sputtered Ti films on indium tin oxide (ITO) films. ITO (also called ITO glass when deposited onto glass substrates) or other transparent conductive films are important in the fabrication of electro-optical and chromic devices. Their conductivity and transparency are the key properties which are utilized in the fabrication of solar cells, displays, optical based chemical and biosensors, as well as many other devices. Knowing how to control the specifications of nanostructured metal oxide films, such as nanotubular TiO₂ layers, which are formed onto these transparent and conductive substrates, is the key for the successful fabrication of the electro-optical and chromic devices.

The formation of nanotubes in Ti films deposited onto ITO glass substrates will be investigated. It will be shown that the results are remarkably different for room and high temperature deposited films and that the deposition temperature plays an important role in the end product.

Anodization Process

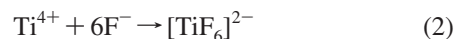
Mor et al.³⁹ have suggested that Ti anodization occurs as a result of a competition between electrochemical oxide formation and chemical dissolution of oxide by fluoride ions. For anodization, the Ti material should be placed in a conductive electrolyte along with a counter electrode. When there is no F[−] ion in the media, a thin barrier metal oxide is formed on the metal surface as^{22,30}



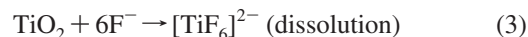
The reaction can be enhanced by the application of an electric field which aids ion transport (O^{2−} and Ti⁴⁺ ions) through the growing oxide. However, as the oxide layer thickness increases in the anodization process, the electric field across the film is progressively reduced. This limits the oxidation process, and eventually the oxidation current (transient current) drops. In this process, Ti⁴⁺ ions, arriving at the oxide/electrolyte interface, are not made soluble by complexation, and a hydroxide layer (Ti(OH)_xO_y) precipitates on the surface. This layer is typically loose and porous, and results in further diffusion-retarding effects.

In the presence of fluoride ions, the situation is different. Fluoride ions impose two effects:

(i) They directly complex with the transported cations at the oxide electrolyte interface (thus preventing Ti(OH)_xO_y precipitation):



(ii) They also have the ability to react with the oxide to form water-soluble [TiF₆]^{2−} complexes (thus, dissolution and breakdown of the barrier layer occurs along a random path through the barrier layer):



This means that the etching will continue, which causes the current increase at the initial stage. Eventually, the rate of titanium oxide growth (eq 1) assisted by electric field equals the rate of dissolution (eqs 2 and 3) by fluoride ions, which results in the constant barrier layer thickness.²² The current eventually decreases due to various effects such as a decrease in the diffusion of fluoride-containing species in and out of the tubes.⁴²

Experimental Section

For this study, titanium films of 1.2 μm thickness were first deposited onto ITO glass substrates using RF sputtering technique from a 99.99% pure Ti target. RF power of 140 W was applied

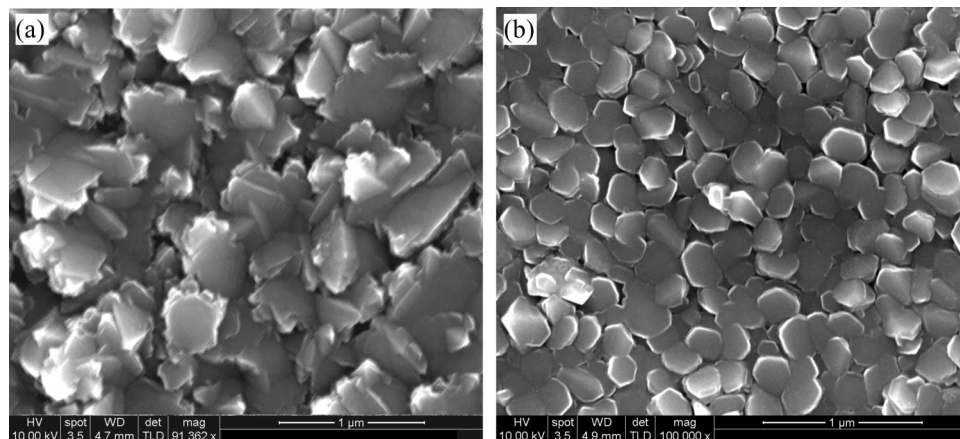


Figure 1. Morphology of RF sputtered Ti films on ITO glass (a) at room temperature and (b) at 300 °C.

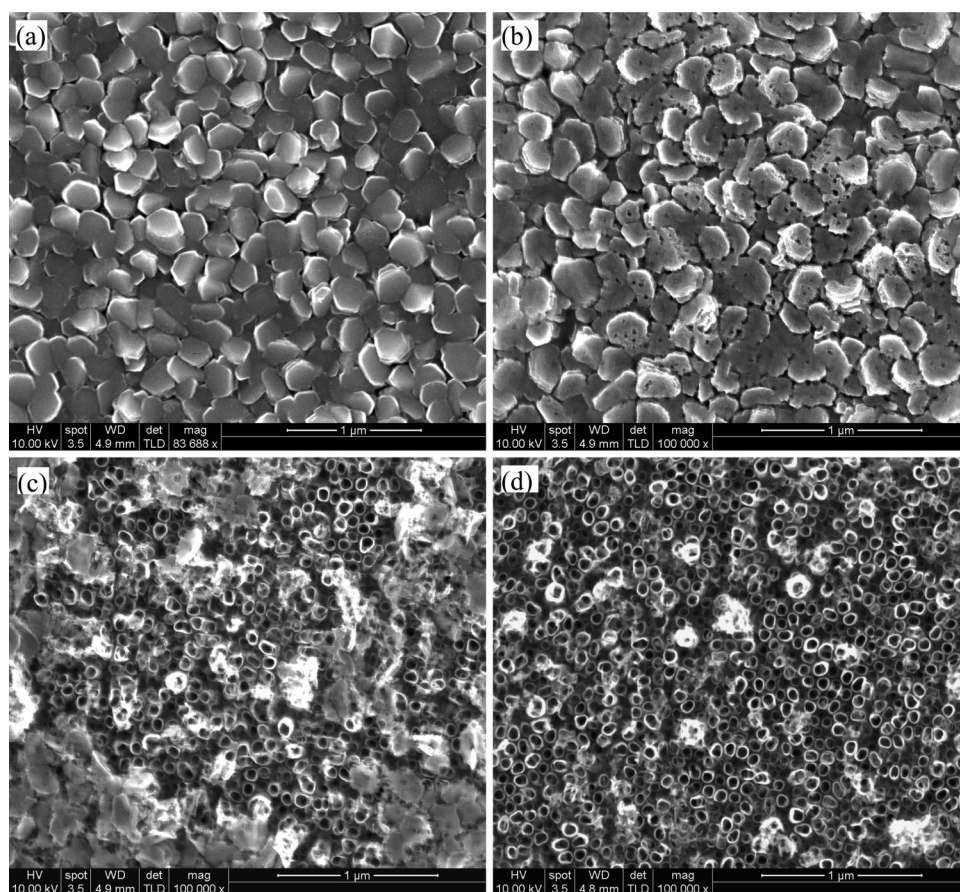


Figure 2. SEM images of 300 °C RF sputtered films at 20 V anodization showing a sequence of steps: (a) after 5 min, (b) after 10 min, (c) after 45 min, and (d) after 80 min.

during the deposition process. The sputtering chamber was pumped down to the background pressure of 10^{-5} torr before introducing the sputtering gas of 100% Ar with a pressure of 2×10^{-2} torr. The substrate temperatures were room temperature and 300 °C, and the deposition time was 60 min.

Anodization was performed in a neutral electrolyte medium of 0.5% (wt) NH_4F /ethylene glycol solution using a platinum foil cathode at room temperature. Nanoporous structure and highly ordered nanotube arrays were grown on respective Ti thin films using anodizing potentials ranging from 3 to 20 V without stirring. Long-term stirring was causing the film to be peeled off during the anodization. Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) spectroscopy were employed to

determine the surface morphology and the crystalline phase of the nanostructured surface.

Results

SEM images of the samples are given in Figures 1–3. From Figure 1, it can be seen that the morphology of the Ti films deposited at room temperature and 300 °C were quite different. The flake-like patterns with jagged circumferences were observed for room temperature deposited Ti (Figure 1a). The film was made of randomly placed platelets on top of each other with dimensions of 100–1000 nm. At elevated temperatures, however, the Ti film formed hexagonal platelets with sides of 100–200

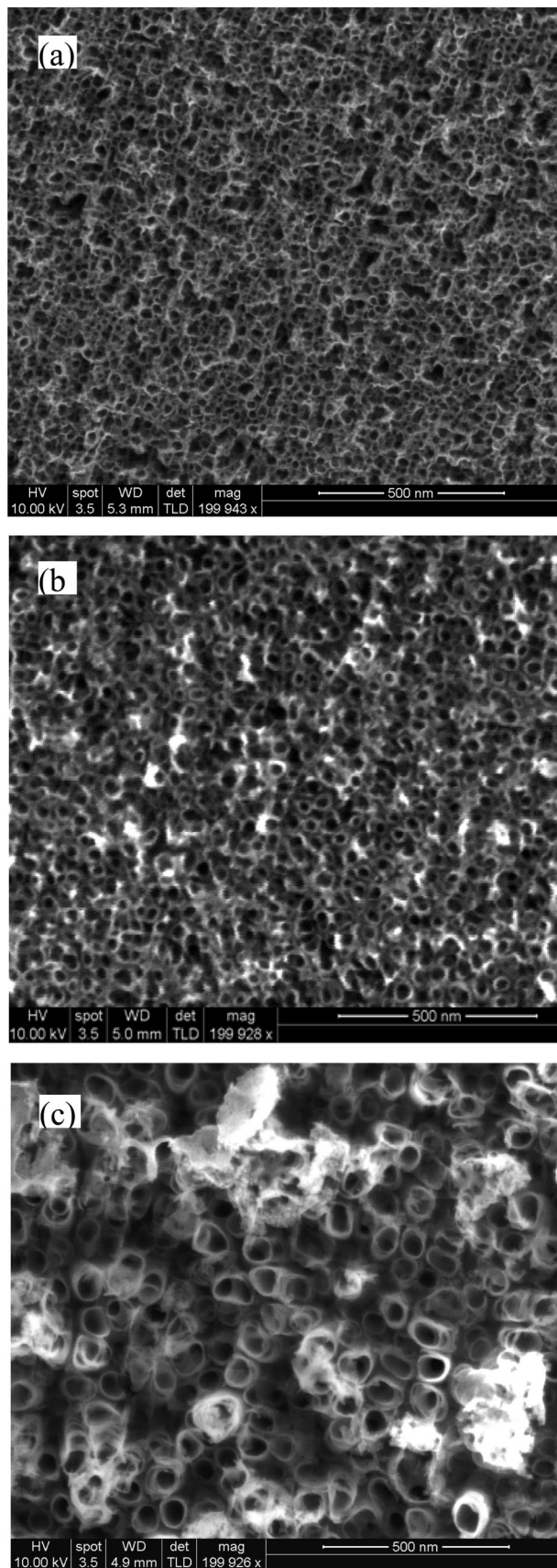


Figure 3. SEM images of 300 °C RF sputtered films on ITO glass with different anodization potentials: (a) 5 V, (b) 10 V, and (c) 20 V (after 80 min of anodization).

nm length and several tens of nm in thickness (Figure 1b). The films formed at the high temperature seemed to have much smoother sides than those formed at room temperature.

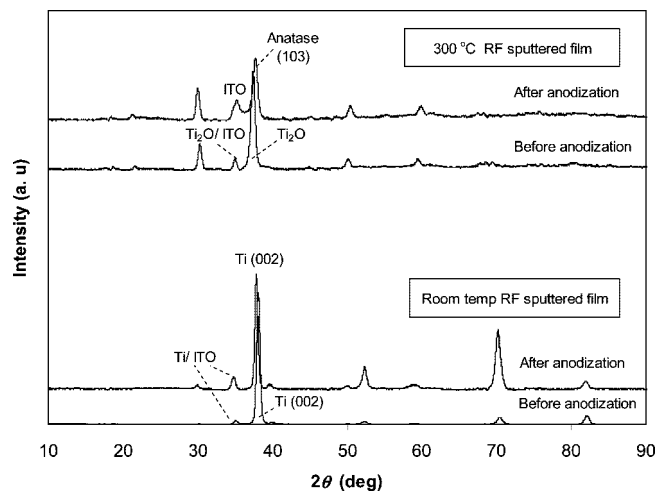


Figure 4. XRD patterns of room temperature and 300 °C RF sputtered films: before and after anodization.

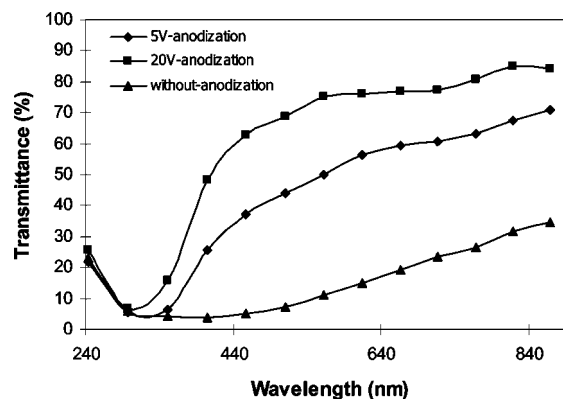


Figure 5. Transmittance spectra of 500 °C annealed Ti films anodized by different voltages.

For room temperature sputtered films, anodization was conducted at different applied potentials ranging from 3 to 20 V. The SEM images of these films (not given) with various applied potentials for 80 min revealed that the anodized thin films sputtered at room temperature have nonuniform and random patterns which were predominantly caused by grain boundary etching and high surface roughness. Anodization with longer duration resulted in more random etching of the films with no significant pattern appearing.

Anodization of 300 °C RF sputtered thin films resulted in well-ordered nanotubes with the diameters being a function of the applied voltage. The anodization processes of the films at 20 V can be seen in Figure 2. When voltage is applied, the film's very top surface is oxidized rapidly (Figure 2a) and transient current decreases from its large initial value and eventually reaches a minimum. Due to the presence of fluoride ions, holes are formed on the Ti surface (Figure 2b) as the anodization continues, and the transient current increases. As the process continues, these holes become larger and the metal oxide barrier layer starts to peel off (Figure 2c). Eventually, the barrier layer is completely removed (transient current reaches a peak value) and the classic Ti anodization occurs with a nanotubular pattern (Figure 2d). Subsequently, the transient current decreases when the tubes become deeper and the diffusion of fluoride-containing species in and out of the tubes becomes more cumbersome.

In the anodization of Ti foils, the applied voltage plays an important role in controlling the tube size. The same is also

observed for the anodization of 300 °C RF sputtered Ti films: the higher the voltage, the larger the diameter of the tubes. It is approximately 10 nm for 5 V and 20 nm for 10 V, while the tube diameter is approximately 45 nm for 20 V (Figure 3). In contrast, the diameters of the nanotubes were almost half of those which were obtained in Ti foils with the same anodization conditions.^{36,37,52} The diameters are similar to those reported by Mor et al.⁴⁷ (20–30 nm with an anodization potential of 10 V) but smaller than those obtained by Macak et al.⁴⁸ on Ti ion-beam deposited film onto Si substrates using HF-containing electrolyte.

As previously described, the high temperature sputtered films are made of hexagonally shaped grains which are highly ordered and are very different from those of the room temperature grain morphologies (Figure 1). It can be seen (Figure 2) that at the start of the anodization process perpendicular holes are formed into these hexagonal surfaces in high temperature deposited films. These holes are homogeneously distributed, which eventually initiate the well-ordered nanotubes. The same pattern is not seen for the room temperature deposited films. For room temperature films, etching starts in the grain boundaries and gradually expands toward different directions. However, some randomly oriented nanopores and short tubes were observed within grain boundaries. It is possible to assume that the starting morphologies play an important role in the formation of well-ordered nanotubes in thin films.

XRD patterns obtained for the room and 300 °C temperature sputtered films before and after anodization are given in Figure 4. Owing to the penetration depth of the X-ray beam, peaks from the ITO substrate (ICDD pattern no. [88-0773], $\text{In}_4\text{Sn}_3\text{O}_{12}$) are present in all spectra. These occur at 18.8, 21.6, 30.4, 35.0, 50.4, and 59.8° 2 θ . Diffraction from the substrate also contributes to the peaks at 35.2, 52.7, and 82.4° 2 θ . Inexplicably, the ITO peaks appear more dominant in the XRD spectra of the 300 °C samples.

The presence of titanium was confirmed in both of the room temperature samples (anodized and nonanodized). Peaks corresponding to the majority of positions for ICDD pattern no. [44-1294] (titanium) were present in both, but with slightly different intensity ratios. The most important difference was that the 100% peak (d_{max}) occurs at 38.3° 2 θ instead of 40.2° 2 θ in the reference pattern. Thus, there is some evidence of preferred orientation for the 002 plane instead of the 101 plane. There is no real evidence for the presence of titanium oxide of any type in the room temperature anodized sample (Figure 4).

In contrast to the room temperature samples, there is no real evidence for the presence of pure Ti in either sample (anodized and nonanodized) (Figure 4), which suggests that partial oxidation of the Ti may have occurred in the 300 °C sample during deposition. Here, the intense peak at 37.2° 2 θ , together with the peak at 34.9° 2 θ , matches well with ICDD pattern no. [11-0218] (Ti_2O_3). The sputtering chamber was empty of oxygen as the sputtering process was conducted in the presence of Ar. The only available source of oxygen was the ITO film. Apparently, during the high temperature deposition process, the ITO film donated oxygen to the Ti film to form Ti_2O_3 . This was confirmed by heating the ITO film at 300 °C in the presence of Ar. A decrease in the conductivity of the film proved a partial reduction of the ITO film. There could be some contribution from Ti to the peak at 35°, and the shoulder at 37.7° 2 θ , but the peaks at 40.2, 52.7, and 70.7° 2 θ are also absent in both. The presence of the oxidized form of titanium in the high temperature deposition was also confirmed by conductivity measurements, as the conductivity of the film was lower than that of the Ti deposited film at room temperature.

In the anodized sample, anatase is clearly present (Figure 4). Apparently, the presence of Ti_2O_3 promotes the formation of anatase and full oxidation of the tubes during the anodization. On matching to ICDD pattern no. [21-1272], we see that the peak at 25.2° 2 θ is absent (101 plane, and usually d_{max}), as are many of the more minor peaks. The peak of maximum reflection occurs at 37.04° 2 θ , which correspond to the 103 plane. Photocurrent measurements which are presented in the next section also confirm the presence of anatase.

Mor et al.⁴⁷ and Yang et al.^{49,50} have reported the presence of well-ordered nanotubes on films sputter deposited at high temperatures (500 °C). Macak et al.⁴⁸ obtained well-ordered nanotubes in ion-beam sputtered films which were obtained at room temperature and low deposition pressure of 10^{-4} torr. However, these groups did not report any relevance between the XRD patterns and the end result in the anodization process. From our aforementioned XRD patterns, it is clear that the lattice structures for the starting material are different for the room temperature and high temperature deposited films. In addition to the initial differences in the surface morphologies (Figure 1), it is also possible that the presence of Ti_2O_3 may promote the formation of well-ordered nanotubes.

Photocurrent Measurements. Photocurrent measurements were conducted to confirm the presence of anatase in the anodized high temperature sputtered films before annealing. Two samples were anodized at 20 V for 80 min. One was annealed at 500 °C for 4 h. They were both placed in a 0.1 M Na_2SO_4 solution against a platinum reference electrode at 2 V. Consequently, they were irradiated by using a 1000 W Xe lamp. The nonannealed sample current was 110 $\mu\text{A}/\text{cm}^2$, and the annealed sample was 30 $\mu\text{A}/\text{cm}^2$. According to the report by Ghicov et al.,⁵⁸ the photocurrent is in the tens of $\mu\text{A}/\text{cm}^2$ range if anatase TiO_2 is present in nanotubular samples, unless the photocurrent is only in the nA/cm² range. Our measurement confirms the presence of the anatase form of TiO_2 even before annealing the samples. The larger current of the nonannealed sample might be due to the presence of partially oxidized Ti underneath the nanotubes which provides a lower resistance for the electronic loop. In addition, annealing at high temperature produces the rutile form of TiO_2 , which is less active than the anatase form.^{11,42}

UV–Vis Spectra. UV–vis transmission spectra of thin films deposited at 300 °C are shown in Figure 5. Three films were chosen: anodized at 5 V, anodized at 20 V, and nonanodized. They were annealed at 500 °C for 4 h in the presence of 90% O_2 and 10% N_2 . After annealing, the already semitransparent 20 V anodized samples became fully transparent but the nonanodized Ti film turned semitransparent. The transparency of the 5 V anodized film was in between them. Apparently, the size of the tubes affects the oxidation time, as the oxygen molecules can diffuse more rapidly when tubes have larger diameters. As can be seen, there is sharp decline in transmittance for wavelengths of less than 400 nm, which is the evidence for the presence of TiO_2 . It has been shown that the nanotubular surfaces transform into the rutile form after annealing at elevated temperatures in the presence of oxygen.^{47,59}

Conclusion

RF sputtered titanium thin films deposited on ITO substrates have been anodized and studied. A neutral electrolyte (ethylene

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glycol) containing 0.5% (wt) NH_4F was used in the process. The study shows that elevated temperature sputtered films are favorable for the formation of well-ordered nanotubes. Anodization of room temperature sputtered films results in irregular film etching. It was observed that 300 °C temperature deposited thin films were poorly oxidized form of Ti (Ti_2O) which may promote the formation of well-ordered anatase titanium oxide

nanotubes during anodization. The presence of anatase was confirmed by XRD and photocurrent measurements. It is suggested that the formation of Ti_2O during the high temperature deposition is due to migration of oxygen from ITO into the Ti film.

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