Research Article

Improved Performance for Dye-Sensitized Solar Cells Using a Compact TiO$_2$ Layer Grown by Sputtering

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This work determines the effect of compact TiO$_2$ layers that are deposited onto fluorine-doped tin oxide (FTO), to improve the performance of dye-sensitized solar cells (DSSC). A series of compact TiO$_2$ layers are prepared using radio frequency (rf) reactive magnetron sputtering. The films are characterized using X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and UV-Vis spectroscopy. The results show that when the Ar/O$_2$/N$_2$ flow rates are 36:18:9, the photo-induced decomposition of methylene blue and photo-induced hydrophilicity are enhanced. After annealing at 450°C in an atmosphere ambient for 30 min, the compact TiO$_2$ layers exhibit higher optical transmittance. The XRD patterns for the TiO$_2$ films for FTO/glass show a good crystalline structure and anatase (101) diffraction peaks, which demonstrate a higher crystallinity than the ITO/glass films. As a result of this increase in the short circuit photocurrent density, the open-circuit photovoltage, and the fill factor, the DSSC with the FTO/glass and Pt counter electrode demonstrates a solar conversion efficiency of 7.65%.

1. Introduction

Photocatalytic TiO$_2$ materials are widely used in antipollution applications, deodorization, dust-proofing, and for high-performance dye-sensitized solar cells (DSSC) because of their unique physical, chemical, and optical properties, their lack of toxicity, and low cost [1]. The energy gap for titanium dioxide for photocatalysts is about 3.2 eV, so ultraviolet excitation causes electrons to jump to the conduction band to form electron-hole pairs. The holes formed in the catalyst are used to degrade organic materials or undesired pollutants for antipollution, deodorization, and antibacterial uses [2, 3]. Because N-doped TiO$_2$ (TiO$_2$:N) powders or thin films have better photocatalytic properties than undoped TiO$_2$ films [4], some studies have added nitrogen gas during the growth of TiO$_2$ films, to increase the photocatalytic activity of TiO$_2$ in the visible-light region [5, 6]. Using N-doped TiO$_2$ results in significant improvements in the visible light response and photocatalytic degradation [7].

Since the first report of a DSSC by O’Regan and Grätzel, in 1991 [8], they have been intensively studied as a potential replacement for standard solar cells because of their relatively high efficiency and low cost [9], compared with p-n junction photovoltaic devices [10, 11]. A typical DSSC consists of dye molecules that act as sensitizers, a porous TiO$_2$ layer, a fluorine-doped tin oxide (FTO) substrate, an electrolyte charge carrier, and a platinized FTO substrate as a so-called counter electrode or cathode. The structure, morphology and crystalline phases of TiO$_2$ play an important role in the performance of DSSC's. The nano-sized porous structure TiO$_2$ layer is widely used as an electrode in DSSC, to allow a high density of dye molecules to be embedded onto the TiO$_2$ surface and enhance the photo absorption process [12]. However, the porous structure of the TiO$_2$ layer...
can cause an electrical short between the liquid electrolyte and the FTO substrate, which leads to a decrease in cell efficiency. A potential means of preventing recombination is the application of a compact metal-oxide film between the nano-sized porous TiO$_2$ layer and the FTO substrate. Of these metal oxides, TiO$_2$ is the most effective electrolyte blocker and has been extensively studied [13, 14]. This compact layer improves the adhesion of the porous TiO$_2$ to the FTO substrate and provides a larger TiO$_2$/FTO contact area and more effective electron transfer from the porous TiO$_2$ to the FTO by preventing the electron recombination process [15]. A compact TiO$_2$ layer is prepared using many growth techniques, such as sputtering, chemical vapor deposition, spin-coating, or spray pyrolysis. In particular, the compact TiO$_2$ layer produced by sputtering deposition is simple and inexpensive and is widely used in DSSC studies [16,17]. This study determines the carrier blocking effect of a compact TiO$_2$ layer that is deposited onto a FTO substrate, using radio frequency (rf) reactive magnetron sputtering, with a Ti metal target, Ar as the plasma gas and O$_2$ and N$_2$ as the reactive gases. The effect of the Ar/O$_2$/N$_2$ flow ratios on the structure, surface morphology, photocatalytic activity, and DSSC conversion efficiency of TiO$_2$ thin films is studied. The nano-sized porous TiO$_2$ layer is coated using the sol-gel process and calcination at 450°C and 500°C. The working electrode is a dye-sensitized TiO$_2$ film that is immobilized on a fluorine-doped tin oxide (FTO) substrate. The Pt and carbon counter electrode are coated onto FTO/glass substrates.

2. Experiments

Compact TiO$_2$ layers were coated onto FTO/glass substrates (nonalkali glass, 25 × 25 × 1 mm$^3$) by rf reactive magnetron sputtering from a high purity Ti target in an Ar/O$_2$/N$_2$ atmosphere, using a constant sputtering pressure (10 mtorr), rf power (100 W), substrate temperature (300°C) and distance between the substrate and the target (80 mm), and variable flow rates for argon, oxygen, and nitrogen. All of the samples were deposited by rotating the substrate (10 rpm), to ensure good surface morphology. Before deposition, the system was evacuated to a pressure of less than 5.0 × 10$^{-6}$ torr. The detailed deposition conditions are listed in Table 1. The substrates were cleaned, in acetone, using ultrasound, rinsed with deionized water, and dried in nitrogen. Samples 1–3 (TiO$_2$) were deposited in an Ar/O$_2$ atmosphere, without nitrogen gas. Samples 4–12 (TiO$_2$−$x$N$_x$) were deposited in an Ar/O$_2$/N$_2$ atmosphere and nitrogen gas was added in different fractions. The TiO$_2$ films were characterized by their deposition rates, hydrophilic properties, photocatalytic behavior, and morphology.

The porous TiO$_2$ film was coated onto the compact TiO$_2$/FTO/glass using a mixture of P-25 with the TiO$_2$ sol-gel component studied in [18,19]. The TiO$_2$ sol-gel was mixed with 0.3 g of commercially available Degussa P-25, to avoid any cracking of the film. The gels were predried for 20 min at 50°C and then sintered in a furnace at 450°C and 500°C (heating rate 10°C/min) for 30 min in air ambient, to produce the bare TiO$_2$ electrode used in this work to fabricate the

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ar flow rate (mL/min)</th>
<th>O$_2$ flow rate (mL/min)</th>
<th>N$_2$ flow rate (mL/min)</th>
<th>Ar:O$_2$:N$_2$</th>
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</thead>
<tbody>
<tr>
<td>Number 1</td>
<td>35</td>
<td>35</td>
<td>0</td>
<td>1:1:0</td>
</tr>
<tr>
<td>Number 2</td>
<td>48</td>
<td>24</td>
<td>0</td>
<td>2:1:0</td>
</tr>
<tr>
<td>Number 3</td>
<td>54</td>
<td>18</td>
<td>0</td>
<td>3:1:0</td>
</tr>
<tr>
<td>Number 4</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>1:1:1</td>
</tr>
<tr>
<td>Number 5</td>
<td>29</td>
<td>29</td>
<td>14</td>
<td>1:1:0.5</td>
</tr>
<tr>
<td>Number 6</td>
<td>25</td>
<td>25</td>
<td>8</td>
<td>1:1:0.33</td>
</tr>
<tr>
<td>Number 7</td>
<td>27</td>
<td>14</td>
<td>14</td>
<td>2:1:1</td>
</tr>
<tr>
<td>Number 8</td>
<td>36</td>
<td>18</td>
<td>9</td>
<td>2:1:0.5</td>
</tr>
<tr>
<td>Number 9</td>
<td>36</td>
<td>18</td>
<td>6</td>
<td>2:1:0.33</td>
</tr>
<tr>
<td>Number 10</td>
<td>45</td>
<td>14</td>
<td>14</td>
<td>3:1:1</td>
</tr>
<tr>
<td>Number 11</td>
<td>45</td>
<td>15</td>
<td>7</td>
<td>3:1:0.5</td>
</tr>
<tr>
<td>Number 12</td>
<td>41</td>
<td>14</td>
<td>4</td>
<td>3:1:0.33</td>
</tr>
</tbody>
</table>

Table 1: The deposition conditions for TiO$_2$.
DSSC. The porous TiO₂ films were immersed into the dye (N 719) complex, for 24 h at room temperature [20, 21].

The Pt and carbon counter electrode was coated onto FTO/glass substrates using DC sputtering with pure Ar gas and a DC power of 30 W. The dye-adsorbed TiO₂ working electrode and the counter electrode were assembled into a sandwich-type cell and sealed with a hot-melt sealant. Figure 1 shows a schematic diagram of a DSSC with a sputtered compact TiO₂ layer/FTO/glass. Dense TiO₂ passivating layers were used to prevent any leakage to the liquid electrolyte by electron transfer.

The photo-induced hydrophilicity was evaluated using contact angle measurements to pure water, which were performed at room temperature in an ambient atmosphere, using a contact angle meter (FACE CA-VP150) with an experimental error of less than 1°. The photocatalytic behavior of the TiO₂ coatings was assessed using a combination of ultraviolet irradiation and absorption measurements. The TiO₂ was placed in 10 μM methylene blue (MB) aqueous solution and irradiated for 4 hours, using 1.5 mW/cm² UV lights. The observed photodecomposition of the aqueous solution is seen in the UV-Vis spectrum (measured using a UVP UVL-225D with a wavelength range of 300–800 nm) as a decrease in the maximum absorbance as the irradiation increases. The film thickness and crystal structure were, respectively, measured using α-step (surface profiler system, Dektat) and XRD (Rigaku-2000). The morphology and the roughness were determined using SEM (JEOL JSM-6500F) and AFM (SPA 400).

The power used to test the prepared DSSC was a 150 W Xe lamp, which simulates sunlight (AM 1.5). Before the test, the distance between the light source and the sample was adjusted to allow a light source density of 100 mW/cm². The cell performance parameters, including the short-circuit current density (Jₘ.), the open-circuit voltage (Vₘ.), the fill factor (FF), and the photoelectronic conversion efficiency (η (%) = Jₘ.×Vₘ.×FF/total incident energy × 100), were measured and calculated using the J-V characteristics of DSSC’s.

### 3. Results and Discussion


The TiO₂ photocatalytic thin films deposited on glass substrates demonstrate very good adherence. No cracking or peel off is observed after deposition. Figure 2 shows the deposition rates for samples number 1, number 2, and number 3. These three samples (where nitrogen was added) were deposited using O₂ flow-rate ratios from 35 to 18 mL/min (see Table 1). The deposition rate increases as the O₂ partial pressure decreases. Greater oxygen flow increases the probability of collision with Ar⁺ ions and decreases the energy of the Ar⁺ ions that bombard the Ti surface. Increasing the O₂ flow rate also results in a significant decrease in the sputtering voltage [22]. Therefore, the dissociation gas is reduced, along with the plasma density and the deposition rate. Table 2 shows the deposition rates and roughness values for all samples. For nitrogen-doped samples, the roughness is increased when the Ar flow fraction is increased.
Figure 3(a) shows the absorption spectrum for MB under UV irradiation for 4 h, for films deposited under various coating conditions. If no nitrogen is added during the deposition process, the best degradation of MB is demonstrated by sample number 2, with a MB absorbance of 0.74. When nitrogen is added during the deposition process, the best absorbance of MB is 0.54, for sample number 8. The deposition parameters for sample number 8 are a rf power of 100 W, a deposition pressure of 10 mtorr, an Ar/O₂/N₂ flow rate of 36/18/9 mL/min, and substrate temperature of 300°C. Figure 3(b) shows the absorption spectrum of MB under visible light irradiation for 4 h for the deposited film samples number 2 and number 8. This result shows that TiO₂−ₓNₓ exhibits photocatalytic characteristics and the MB degradation of TiO₂−ₓNₓ film is better than that of TiO₂ film.

Figures 4(a) and 4(b) show the change in the water contact angle after UV irradiation for 9 min, without and with the addition of nitrogen, respectively. Figure 4(a) shows that the contact angles for the TiO₂ films decrease by 1°, 14°, and 13°, for samples number 1, number 2 and, number 3, respectively, after UV irradiation for 9 min. Figure 4(b) shows that the average contact angle for TiO₂−ₓNₓ film deposited...
with the addition of nitrogen is 20° less after UV irradiation. This result shows that the photo-induced hydrophilicity of TiO$_{2-x}$N$_x$ film is better than that of TiO$_2$ film. The best degradation occurs for samples number 2 and number 8, without and with nitrogen addition, respectively, as determined by AFM and SEM. Figures 5 and 6 show the morphology of samples number 2 and number 8, respectively. The columnar structures of the two films are identified using AFM. The respective roughness ($R_a$) values for samples number 2 and number 8 are 0.33 nm and 1.21 nm (see Table 2). The atomic number ratio for the surface and the volume is an important parameter for photocatalytic properties. A higher ratio results in greater photocatalytic activity. When the roughness value decreases, the photocatalytic activity decreases, because there is less surface area. In contrast, when the roughness is greater, the photocatalytic activity is greater, because there is a larger surface area.

3.2. DSSC Characterization. Figure 7 shows the transmittance spectra as a function of wavelengths in the visible range for compact TiO$_2$ layers. After annealing at 450°C in an atmosphere ambient for 30 min, the compact TiO$_2$ layers demonstrate higher optical transmittance. However, when the annealing temperature is 500°C, the optical transmittance decreases slightly.

SEM analysis was used to determine the morphology of the TiO$_2$ porous layer produced using the sol-gel method onto the compact TiO$_2$ layers (sputtered with Ar/O$_2$/N$_2$ flow rates of 36:18:9: sample number 8)/FTO substrate, as shown in Figure 8. The samples were annealed at 450°C in an atmosphere ambient for 30 min. After sputtering the compact TiO$_2$ layers are dense and evenly coated to prevent charge recombination, which adheres to the electrode surface strongly (Figure 8(a)). The SEM images show the porous TiO$_2$ film over the sputtered compact layer that is produced using sol-gel with spin coating has proper density and the crystallite size (Figure 8(b)), which gives a more efficient DSSC. The cross-section of the films was observed by SEM. Figure 9(a) corresponds to Figure 8(b) and Figure 9(b) corresponds to Figure 8(c). These results confirm a sponge-like structure for the TiO$_2$ layer, which is a prerequisite for a highly efficient DSSC. Figure 10 shows the XRD patterns.
Figure 7: The optical transmittance spectra for a compact TiO$_2$ layer/FTO/glass.

for the TiO$_2$ films. FTO/glass shows a good crystalline structure and anatase (101) diffraction peaks that have a higher crystallinity than the ITO/glass films.

In order to compare the performance of a DSSC fabricated on the FTO/glass substrate and the ITO/glass substrate, using Pt counter electrodes and carbon counter electrodes [23], a conventional DSSC was prepared, as shown in Figure 11. Figure 11 shows the photocurrent-voltage (J-V) characterization of the DSSC with a sputtered compact TiO$_2$ layer, under AM 1.5 solar irradiation with a density of 100 mW/cm$^2$. The performance parameters are summarized in Table 3. The short circuit photocurrent density ($J_{sc}$), the open-circuit photovoltage ($V_{oc}$), and the fill factor for the FTO/glass substrate using Pt counter electrodes are greater than those for the other samples. With ITO/glass, using the carbon counter electrodes, conversion efficiency decreases to 1.51%, from 4.98%, for Pt counter electrodes. This increase in the $J_{sc}$, the $V_{oc}$, and the fill factor means that the DSSC with the FTO/glass and a Pt counter electrode has a solar conversion efficiency of 7.65%, compared with 4.98% for the cell prepared using ITO/glass.

4. Conclusions

This study successfully deposits TiO$_2$ and TiO$_{2-x}$N$_x$ onto ITO/glass and FTO/glass substrates. The flow rates for Ar (plasma gas), O$_2$, and N$_2$ (reactive gases) are varied, but the rf power, the deposition pressure, and the substrate temperature are fixed. The results show that the photo-induced hydrophilicity of TiO$_{2-x}$N$_x$ film is better than that of TiO$_2$ film. The best absorbance of methylene blue (MB) is 0.54, for sample number 8 (the Ar/O$_2$/N$_2$ flow rates are 36:18:9), after UV irradiation for 4 h. This result shows that MB degradation for TiO$_{2-x}$N$_x$ film is better than that for TiO$_2$ film. After annealing, the compact TiO$_2$ layers exhibit higher optical transmittance. The TiO$_2$ porous layer on the TiO$_2$ compact layers/FTO substrate produced using the sol-gel method exhibits a sponge-like structure, which is a prerequisite for a highly efficient DSSC. For ITO/glass with carbon counter electrodes, the conversion efficiency decreases to 1.51%, from 4.98% for Pt counter electrodes. The short circuit photocurrent density ($J_{sc}$), the open-circuit
photovoltage \( V_{oc} \), and the fill factor for the FTO/glass substrate with Pt counter electrodes are greater than those of the other samples.

**Figure 9:** The SEM cross-sectional image (a) corresponding to Figure 8(b) and (b) corresponding to Figure 8(c).

**Figure 10:** The XRD patterns for the TiO\(_2\) films, annealed at 450°C.

**Figure 11:** Current-voltage plots for the DSSC with a sputtered compact TiO\(_2\) layer, using carbon and Pt counter electrodes and FTO and ITO/glass, under AM 1.5 solar irradiation with a density of 100 mW/cm\(^2\) (TiO\(_2\) annealed at 450°C).
Table 3: Photovoltaic performance of DSSCs with sputtered compact TiO\textsubscript{2} layer, with carbon and Pt counter electrodes, using FTO and ITO/glass.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm(^2))</th>
<th>Fill factor</th>
<th>Efficiency $\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO/sputter/spin coating/Pt</td>
<td>0.762</td>
<td>13.95</td>
<td>0.720</td>
<td>7.65</td>
</tr>
<tr>
<td>ITO/sputter/spin coating/Pt</td>
<td>0.622</td>
<td>12.38</td>
<td>0.647</td>
<td>4.98</td>
</tr>
<tr>
<td>ITO/sputter/spin coating/carbon</td>
<td>0.522</td>
<td>4.33</td>
<td>0.668</td>
<td>1.51</td>
</tr>
</tbody>
</table>

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**References**


