Improved performance of dye-sensitized solar cells with compact TiO$_2$ blocking layer prepared using low-temperature reactive ICP-assisted DC magnetron sputtering

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Abstract

This study discusses about carrier blocking effects of a compact TiO$_2$ deposited onto fluorine-doped tin oxide (FTO) to improve the performance of dye-sensitized solar cells (DSSCs). The compact TiO$_2$ blocking layer is prepared by reactive inductively coupled plasma (ICP)-assisted DC magnetron sputtering without substrate heating. The resulting layer yields a 47% improvement in the energy conversion efficiency, indicating that the blocking layer prepared by low temperature ICP-assisted sputtering effectively prevents physical contact with the FTO. This process may suggest a new method for fabricating photoelectrodes which consist of TiO$_2$ blocking layer for use in flexible DSSCs.

1. Introduction

Since the first report of low-cost dye-sensitized solar cells (DSSCs) in 1991 by O’Regan and Grätzel [1], DSSCs have been regarded as the next-generation solar cells [2–8]. DSSCs consist of dye molecules acting as sensitizers, a porous TiO$_2$ layer, a fluorine-doped tin oxide (FTO) substrate, an electrolyte charge carrier, and a Pt-coated counter electrode. Unidirectional charge flow is an essential prerequisite for high energy conversion efficiencies. Four significant interfaces play a role in the unidirectional electron transport in DSSCs: porous-TiO$_2$ layer/dye molecule interface, FTO/porous-TiO$_2$ layer interface, dye molecule/electrolyte interface, and electrolyte/Pt-coated counter electrode interface. Among these, charge recombination processes that interfere with unidirectional electron transport occur mainly at the porous TiO$_2$ layer/dye molecule and FTO/porous TiO$_2$ layer interfaces. However, the recombination at the porous TiO$_2$ layer/dye molecule interface is insignificant [9,10], because the injection of photoelectrons from dye molecules is significantly faster than the charge transfer from TiO$_2$ to the oxidized dye molecules.

On the other hand, at the FTO/porous TiO$_2$ layer interface, charge recombination takes place due to the physical contact between the electrolyte and the surface of the FTO substrate. The porous structure of the TiO$_2$ layer permits electrolyte to percolate into the FTO surface, providing bare FTO conducting sites at which the injected electrons can recombine with I$_3^-$ species from the redox electrolyte. Therefore, suppression of electron leakage on the FTO/porous TiO$_2$ layer interface plays an important role in improving the energy conversion efficiency of DSSCs.

A promising method for preventing recombination is the application of a compact metal oxide blocking layer between the FTO and the porous TiO$_2$ layer [11,12]. Much research has been devoted to the fabrication of compact metal oxide layers that can be used as blocking layers to impede electrolyte invasion. Various metal oxides, including TiO$_2$ [13–15], ZnO [16], and Nb$_2$O$_5$ [17,18], have been used as electrolyte blocking layers at the FTO/porous-TiO$_2$ interface. Among these metal oxides, TiO$_2$ is the most effective electrolyte blocker, and has been extensively studied. Moreover, enhanced adherence between the FTO substrate and the porous-TiO$_2$ layer provides a great number of pathways for photo-excited electron transport from the porous TiO$_2$ to the FTO, which promote electron transfer and enhance the electron transfer efficiency.

The compact TiO$_2$ layer can be prepared using sol–gel processing [13], dip-coating [19], spray pyrolysis [12,15,20], layer-by-layer processing [10], and other techniques. Despite improvements in the energy conversion efficiency with these techniques, high-temperature heat treatments and difficulties associated with large-scale fabrication limit the utility of these methods. Although compact blocking layers prepared at low temperatures, using microwaves has been studied [21], the
resulting cells yielded lower energy conversion efficiencies than those prepared at high temperatures. On the basis of this point, reactive inductively coupled plasma (ICP)-assisted DC magnetron sputtering may provide a more attractive process because it produces a uniform thickness, can be applied to large size substrates, and provides good crystallinity. To our knowledge, this is the first report of the preparation of compact TiO$_2$ blocking layers via low-temperature reactive ICP-assisted DC magnetron sputtering for DSSCs.

In this study, we investigated the carrier blocking effects of a compact TiO$_2$ layer deposited onto a fluorine-doped tin oxide (FTO) substrate as a function of the TiO$_2$ layer thickness. The compact TiO$_2$ blocking layer was prepared by using low temperature reactive ICP-assisted DC magnetron sputtering without intentional substrate heating. The temperature of the substrate was maintained below 150°C with water cooling. The placement of the compact TiO$_2$ blocking layer deposited by ICP-assisted DC magnetron sputtering between the FTO and the porous TiO$_2$ layer was selected to reduce electron recombination at the FTO/porous TiO$_2$ interface, and thereby increasing the DSSC performance in terms of the open-circuit voltage ($V_{oc}$) and the short-circuit current ($I_{sc}$). Optimization of the TiO$_2$ blocking layer thickness is reported in this paper.

2. Experimental

2.1. Preparation of the compact TiO$_2$ layer

Fig. 1 shows a schematic diagram of the process of ICP-assisted DC magnetron sputtering with target voltage control. A two-turn antenna shielded by an insulator, which was made of copper to enable water cooling, was coupled to a 13.56 MHz radio frequency (RF) power generator. The opposite end of the RF coil was connected to the ground. The target was a 3 in. diameter metallic Ti (99.9%) plate positioned 4 in. from the substrate, and was mounted on the magnetron. Transparent FTO (Pilkington, TEC-8, 8 Ω cm$^{-2}$) was used as the substrate and was not subjected to additional heating. The chamber was evacuated to a base pressure of 5.0 × 10$^{-5}$ Pa, then the chamber was purged with Ar. The working pressure was 2.67 Pa (20 mTorr), and the RF power applied to the coil was 400 W. A constant DC power of 400 W was applied to the target, and the target voltage was controlled by varying the oxygen flow rate using a proportional integral derivative (PID) controller. In this paper, BL x denotes a compact TiO$_2$ blocking layer (BL) of thickness x deposited on the FTO substrate.

2.2. Characterization of the compact TiO$_2$ layer

The microstructures of the compact TiO$_2$ layers were examined using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6330F), and the crystal structures of the TiO$_2$ layer were determined using wide-angle X-ray diffraction (XRD, MAC/Sci. MXP 18XHF-22SRA with Cu Kα radiation) at room temperature. An accelerating voltage of 50 kV and an emission current of 100 mA were used. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 5000 VersaProbe (Ulvac-PHI). The background pressure was 6.7 × 10$^{-8}$ Pa, and the anode generated an Al Kx X-ray beam of 15 kV (photon energy of 1486.8 eV). The thicknesses of the TiO$_2$ layer were measured using an α-step profiler. The optical transmittances of the TiO$_2$ blocking layers were determined by ultraviolet–visible (UV/Vis) spectroscopy.

2.3. Fabrication of DSSCs

The FTO substrates with blocking layers were coated with nanocrystalline TiO$_2$ (Nanoxide D, Soloronix, 5 μm). For comparison, an FTO substrate without a blocking layer (blank sample) was also prepared using the same method, and the cell components were then sintered 500°C for 30 min. The annealed electrodes were immersed in ethanol containing a 0.5 mM of dye (NT719, Soloronix) solution for 24 h. Electrodes coated with adsorbed dye were rinsed with anhydrous acetonitrile. Each counter electrode was fabricated by coating a Pt layer onto an FTO substrate by spin-coating a H$_2$PtCl$_6$ isopropanol solution, followed by heating at 400°C for 20 min. The working and counter electrodes were sealed with a Surlyn tape of thickness 25 μm, and then immersed in a redox electrolyte containing 0.7 M 1-butyl-3-methylimidazolium iodide (BMII), 0.03 M iodine, 0.5 M tert-butylpyridine (tBP), and 0.1 M guanidine thiocyanate (GSCN) in acetonitrile/valeronitrile (8.5:1.5 by volume ratio), thereby producing the DSSCs. In this study, D- BL x denotes a DSSC prepared using a compact TiO$_2$ blocking layer of thickness x.

2.4. Photovoltaic and electrochemical characterization of DSSCs

The photovoltaic properties of DSSCs were determined using a Keithley 2400 source measuring unit. A Xe lamp (Oriel, 300 W) served as the light source and its light intensity was adjusted using a Si reference DSSC equipped with a KG-5 filter (Fraunhofer Institute, Germany) to approximately AM-1.5, which corresponds to a solar elevation of 42° with respect to the horizon. All DSSC parameters were measured under standard conditions at AM 1.5 global radiation with 100 mW cm$^{-2}$ light intensity.

Cyclic voltammetry was performed in an acetonitrile solution at a scan rate of 100 mV s$^{-1}$. The bare FTO or the compact TiO$_2$ layer on the FTO (BL 100) was used as the working electrode, a Pt foil provided the counter electrode, and an Ag/Ag* electrode provided the reference electrode. An acetonitrile electrolyte solution was used. The solution contained 0.1 M LiClO$_4$ as the supporting electrolyte and 5 mM Li$_3$I$_2$ (Li: I$_2$ = 9:1 by molar ratio) as the redox couple.

3. Results and discussion

3.1. Characterization of the compact TiO$_2$ layer

Fig. 2(a) and (b) shows the target voltage and total pressure curves as functions of the oxygen flow rate, respectively. The hysteresis loops in the target voltage and total pressure curves indicate that the target surface changed from a metallic state to an oxidized state poisoned by an oxide layer depending on the oxygen flow rate. As shown in Fig. 2(a), because the transition between the metallic and oxidized states is irreversible once the surface of the Ti target was poisoned by an oxide layer, the deposition of a compact TiO$_2$ layer by reactive sputtering must be controlled precisely. This result was in good agreement with the results of our previous study [22], which found that a high deposition rate and TiO$_2$ stoichiometry, could be obtained by conducting deposition at an oxygen flow of 2.6–3.0 sccm with the target voltage fixed at
was the relationship and energies characterized could be controlled according to the sputtering time in the range of 0–30 min, and the layer thickness varied from 0 to 400 nm. The relationship between the TiO₂ layer thickness and the sputtering time is shown in Table 1.

Fig. 3 shows the FE-SEM surface morphologies of the FTO substrate and the compact TiO₂ layer on the FTO substrate. The FTO surface had a morphology characteristic of a tin oxide crystal with particles 100–200 nm in size. After sputtering, the smooth surface was observed to change to a rough surface with relatively small particles, which indicated that the FTO substrate was well-covered with a thin compact TiO₂ layer.

XPS measurements were used to examine the valence of the Ti and O species. The sample used for this study was BL 100. The Ti 2p and O 1s XPS spectra are presented in Fig. 4 and the binding energies and atomic concentrations are summarized in Table 2. The Ti 2p₃/₂ and Ti 2p₅/₂ spin–orbital splitting photoelectrons were characterized by binding energies of 465.12 eV and 459.25 eV, respectively. A peak separation of 5.87 eV agreed well with the values reported elsewhere [23,24]. Only the Ti⁴⁺ signal was detectable on the surface, indicating that a TiO₂ layer formed on the FTO surface. The O 1s feature shown in Fig. 5(b) included two peaks, one at 530.5 eV, which corresponded to oxygen in the Ti–O groups, and another smaller signal at 532.25 eV, which corresponded to oxygen in the OH⁻ groups. Thus, the Ti species in the compact TiO₂ were Ti⁴⁺ and almost all oxygen present was bound to Ti with a titanium-to-oxygen ratio of 0.53:1, in agreement with the expected stoichiometry. Thus TiO₂ was successfully deposited on the FTO substrate.

Fig. 5 shows the XRD patterns of the FTO and the compact TiO₂ layer on the FTO. To accommodate the sensitivity of the XRD measurement, a 1 μm TiO₂ layer was prepared over 75 min of reactive sputtering. A comparison to the bare FTO showed that a new peak appeared at 25.4°, corresponding to the (1 0 1) plane of anatase TiO₂ (JCPDS Card No. 21-1272) without the use of heat treatments. The formation of this crystalline phase was attributed to the use of high-density plasma.

Table 1

<table>
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<th>Sample name</th>
<th>Sputtering time (min)</th>
<th>Compact TiO₂ layer thickness (nm)</th>
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<tr>
<td>Without BL</td>
<td>0</td>
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</tr>
<tr>
<td>BL 50</td>
<td>4</td>
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<td>201</td>
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<td>BL 400</td>
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<td>412</td>
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Table 2

<table>
<thead>
<tr>
<th>Ti</th>
<th>O</th>
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<tr>
<td>Location of binding energy (eV)</td>
<td>Location of binding energy (eV)</td>
</tr>
<tr>
<td>2p₃/₂</td>
<td>2p₅/₂</td>
</tr>
<tr>
<td>465.12</td>
<td>459.25</td>
</tr>
<tr>
<td>Atomic concentration (%)</td>
<td>Atomic concentration (%)</td>
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<td>18.62</td>
<td>33.08</td>
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Fig. 4. High-resolution XPS spectra for the BL 100: (a) the Ti 2p peak and (b) the O 1s peak.

Fig. 6 shows the transmission spectra of compact TiO2 layers on FTO in comparison with the transmittance of a conventional P25 (Degussa) layer with the same thickness (1 μm) in the range from 400 to 700 nm. The compact TiO2 layer on the FTO substrate had an average transmittance of 80% in the visible light region, whereas the conventional P25 layer had a relatively poor transmittance of 20% in the same range. Transparent TiO2 layers in DSSCs increase the light path length (light scattering) and enhance the light harvesting efficiency [25]. Therefore, the deposition of transparent TiO2 blocking layers on FTO is very important.

3.2. Photovoltaic and electrochemical characterization of DSSCs

The photocurrent density–potential curves (J–V) for DSSCs with compact TiO2 layers of various thickness value are presented in Fig. 7(a). The relationship between the TiO2 layer thickness and the open-circuit voltage, Voc, short-circuit current, Jsc, and fill factor (FF) are illustrated in Figs. 7(b)–(d), respectively. The electrical parameters are listed in Table 3. Without a blocking layer, the cell was characterized by Jsc = 10.16 mA cm⁻², Voc = 0.703 V, and FF = 0.61, corresponding to a conversion efficiency of 4.37%. After deposition of a compact TiO2 layer at the FTO/porous-TiO2 interface, the devices yielded improved properties, Voc increased, and high values were observed for 100 nm thick layers. This result suggested that the electron recombination at the FTO interface was prevented for layer thicknesses greater than 100 nm, as shown in Fig. 7(b). Voc of the DSSCs was mainly influenced by two factors: dye loading and charge recombination at the electrode [26–28]. Because the blocking layer itself cannot adsorb significant quantities of the dye, the dye loading must not, therefore, significantly influence Jsc. The main factor that affected Jsc for DSSCs must be the electron back transfer at the FTO/electrolyte interfaces. As shown in Fig. 7(c), the compact TiO2 layer produced by reactive ICP-assisted DC magnetron sputtering reduced the number of recombination sites, and charge recombination in the DSSC was effectively inhibited. An electrode with the compact TiO2 blocking layer decreased electron recombination at the FTO/electrolyte and electron loss at the FTO/porous TiO2, thereby enhancing the electron collection efficiency at the FTO to improve the overall conversion efficiency. Along with an increase in the thickness of the compact TiO2 blocking layer, D-BL 400 gave a low FF of 0.53 with a 5.05% energy conversion efficiency. These results suggested that thick blocking layers introduced an additional series resistance into the devices, which decreased Jsc and FF, as shown in Figs. 7(c) and (d), respectively. The optimal thickness of a blocking layer produced by ICP-assisted reactive TiO2 sputtering was around 100 nm, and the photovoltaic performance of DSSCs was sensitive to the thickness of the compact TiO2 layer. The energy conversion efficiency of D-BL 100 DSSC was lower than the efficiencies of DSSCs reported currently. It should be noted that the purpose of our study was to determine the effect of carrier blocking
on DSSC performance upon introduction of a compact TiO2 layer prepared by low-temperature reactive ICP-assisted DC magnetron sputtering. From this perspective, it is noteworthy that the energy conversion efficiency of a D-BL 100 DSSC with a compact TiO2 layer was 47% higher than that of the reference DSSC without a compact TiO2 layer. The good performance arose from the good electron transport at the electrode interfaces because the FTO surface was well-covered with the compact TiO2 layer.

In general, it is reported that the DSSC performance depends on the dye molecule, the porous-TiO2 layer, an FTO substrate, electrolytes, and a Pt counter electrode, as well as the nature of the blocking layer. Studies are underway to further enhance the performance of DSSCs that include a compact TiO2 layer using newly developed working electrode, and a report will be forthcoming.

A comparison of the dark currents of the investigated cells can provide useful information regarding the back electron transfer processes, and DSSC dark current measurements have been suggested as qualitative method for measuring the extent of back electron transfer [29,30]. Fig. 8 shows the measured dark current–voltage characteristics of DSSCs with and without blocking layers. The onset of a DSSC without blocking layer occurred at a low forward bias. The compact TiO2 blocking layer suppressed the dark current, and shifted its onset by several hundred millivolts. This onset shift indicated that electron recombination at the exposed regions of the FTO substrate was responsible for the high dark currents observed with the porous TiO2 layer alone. These results clearly suggest that the compact TiO2 layer deposited via reactive ICP-assisted DC magnetron sputtering provided an effective

<table>
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<tr>
<th>Sample name</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without BL</td>
<td>0.703</td>
<td>10.16</td>
<td>0.61</td>
<td>4.37</td>
</tr>
<tr>
<td>D-BL 50</td>
<td>0.703</td>
<td>11.61</td>
<td>0.60</td>
<td>4.90</td>
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<tr>
<td>D-BL 100</td>
<td>0.733</td>
<td>13.92</td>
<td>0.63</td>
<td>6.42</td>
</tr>
<tr>
<td>D-BL 200</td>
<td>0.729</td>
<td>13.51</td>
<td>0.57</td>
<td>5.57</td>
</tr>
<tr>
<td>D-BL 400</td>
<td>0.732</td>
<td>12.93</td>
<td>0.53</td>
<td>5.05</td>
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Fig. 7. (a) $J$–$V$ curves of DSSCs with the various TiO2 layer thickness and relationships between the sputtering time and (b) $V_{oc}$, (c) $J_{sc}$, and (d) FF.

Fig. 8. Dark current–voltage characteristics of DSSCs with and without the compact TiO2 blocking layer.
4. Conclusions

Reactive ICP-assisted DC magnetron sputtering without intentional substrate heating was used to deposit a compact TiO₂ layer on an FTO substrate. The thickness of the prepared TiO₂ layer was controlled by varying the sputtering time over the range 0–30 min, and the thickness varied from 0 to 400 nm. The dye-sensitized photoelectrodes displayed improved Voc and Jsc without lowering the FF, which improved the device performance. An optimum TiO₂ blocking layer thickness of 100 nm produced a 47% improvement in the energy conversion efficiency (4.37–6.42%). This indicates that optimizing the thickness of the compact TiO₂ layer is important for obtaining high-performance DSSCs. The compact TiO₂ layer enhanced Jsc and improved adhesion between the FTO and porous TiO₂ layer. Voc was also enhanced, indicating that the compact TiO₂ blocking layer effectively suppressed back electron transfer at the FTO/porous TiO₂ layer interface. Cyclic voltammetry confirmed that the compact TiO₂ blocking layer played an important role in unidirectional electron transport at the interfaces of DSSCs. In summary, low-temperature reactive ICP-assisted DC magnetron sputtering provides a method for fabricating dye-sensitized photoelectrodes based on compact TiO₂ blocking layers, which are expected to be good candidate electrodes in flexible DSSCs.

Acknowledgement

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References