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The effect of RF-sputtered TiO_2 passivating layer on the performance of dye sensitized solar cells

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Abstract

The aim of this work is to prevent the back transfer of electrons due to direct contact between the electrolyte and the conductive substrate by using TiO_2 passivation. A thin TiO_2 passivating layer was deposited on fluorine-doped tin oxide (SnO_2:F, denoted FTO) glass by radio frequency (denoted RF) magnetron sputtering using different working pressures. The thickness and the crystalline structure were adjusted by applying various working conditions. The TiO_2 films calcinated at low working pressure had an anatase phase, and they grew into a rutile phase with a decrease of the working pressure. The dye-sensitized solar cell using TiO_2 passivating layer prepared at 0.5 mTorr was measured the maximum conversion efficiency of 4.6% due to effective prevention of the electron recombination to electrolyte. It was found that the conversion efficiency of the dye sensitized solar cell (denoted DSSC) was highly affected by the crystalline structure of the passivating layer.

Keywords: A. Films; B. Grain size; C. Optical properties; D. TiO_2

1. Introduction

DSSCs have been attracting considerable attention all over the world due to their reasonable conversion efficiency, low production cost and simple fabrication process when compared to silicon solar cells [1]. A unidirectional charge flow with no electron leakage at the interfaces is essential for a high energy conversion efficiency [2]. According to the unidirectional electron transporting principle of DSSCs, there are four important interfaces: the FTO/TiO_2, the TiO_2/dye, the dye/electrolyte, and the electrolyte/counter electrode. Recently, many researchers have paid much attention to the FTO/TiO_2 interface. Mesoporous TiO_2 is commonly used in the DSSCs to embed a high density of dye molecules onto the TiO_2 surface in order to enhance the photoabsorption process. However, the highly porous structure of the TiO_2 layer may cause an electrical short between the liquid electrolyte and the transparent conducting oxide (TCO). To avoid this problem, TiO_2 is widely used as a compact passivating layer in DSSCs [3]. Some researchers have tried to prepare thin TiO_2 blocking (passivating) layers by dry processes, such as the sputtering method [4], and the chemical vapor deposition method [5], which are suitable for forming uniform and fine membranes over a large area with more stable material properties than wet processes. In this work, a TiO_2 passivating layer was deposited onto FTO glass by the RF sputtering with different working pressures and a nanoporous TiO_2 upper layer was prepared by the sol–gel method.

2. Experimental

The passivating TiO_2 under layer was deposited onto FTO by sputtering with an RF magnetron. The target was a TiO_2, 2 in. in diameter and 1/4 in. thick, with a purity of 99.99%. A constant RF power of 80 W was applied to the target. Ar gas was introduced into the chamber at 15 sccm. In order to remove the surface contaminants on the target, pre-sputtering was done for 30 min in pure argon. The crystallite structure of the TiO_2 passivating layer was controlled by an increase in the working pressure at optimized constant conditions. The nanoporous TiO_2 upper layer of a 5 μm thick were coated on the TiO_2

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passivating layer-coated FTO glass using a screen printing method. The films were calcinated in air at 450 °C for 1 h using a programmable furnace to obtain the desired stoichiometry and crystallinity of the TiO_2. The nanoporous TiO_2 films were immersed into the dye (N719) complex for 24 h at room temperature. A counter electrode was prepared by dropping an H_2PtCl_6 solution onto FTO glass and heating at 450 °C for 30 min. The dye-adsorbed TiO_2 electrode and the Pt counter electrode were assembled into a sandwich type cell and sealed with a hot-melt sealant 50 μm thick. An electrolyte solution was introduced through a drilled hole in the counter electrode. The hole was then sealed using a cover glass. The phase identification of the particles obtained at various working pressures was performed by X-ray diffraction (XRD) using a Rigaku D/MAX-2200 diffractometer with Cu Kα radiation. The morphology and the thickness of the prepared TiO_2 passivating layers were investigated using field-emission scanning electron microscopy (FE-SEM, model S-4700, HITACHI). The transmittance of the TiO_2 thin films was measured using a UV spectrometer (UV–vis 8453, Agilent). The conversion efficiency of the fabricated DSSC was measured with a *I–V* Solar simulator (Solar simulator, Oriel).

3. Results and discussion

Fig. 1 shows the XRD patterns of the sputter deposited TiO_2 films. It can be obviously seen from the XRD patterns that the phase structure of the TiO_2 passivating layer at 10 mTorr and 15 mTorr show a prominent anatase peak at 25.4° (1 0 1) and 48° (2 0 0). However, at 5 mTorr, the anatase peaks disappear whereas the intensities of the rutile peaks at 27.4° (1 1 0)

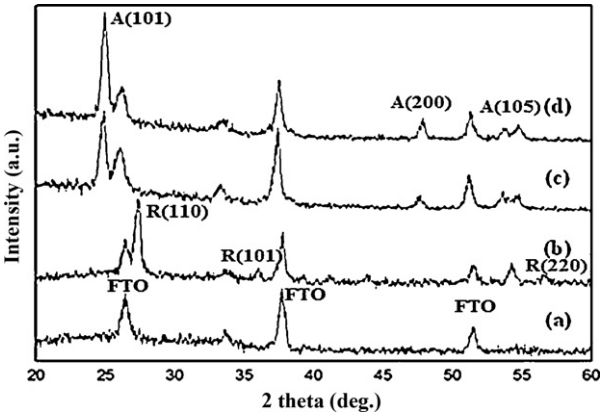

Fig. 1. XRD patterns of the TiO_2 passivating layer (a) plain FTO glass, (b) 5 mTorr, (c) 10 mTorr, and (d) 15 mTorr.

increase. When the working pressures increase, the XRD patterns of the TiO_2 thin films grew anatase peaks (1 1 0). It is evident that the rutile characteristic peaks become anatase peaks as the working pressure increases [6].

The FE-SEM images of TiO_2 passivating layers prepared at various working pressures are shown in Fig. 2. The FE-SEM images reveal that the TiO_2 particles are spherical. The FE-SEM images of the TiO_2 passivating layer prepared at 5 mTorr reveal that the grain size was 35 nm. As the working pressure increased, the grain size became 25 nm. The SEM results show that the grain size of the rutile phase is larger than that of the anatase phase [7].

The cross-sectional FE-SEM image of the TiO_2 passivating layer is shown in Fig. 3. Fig. 3(a) shows cross-section view of

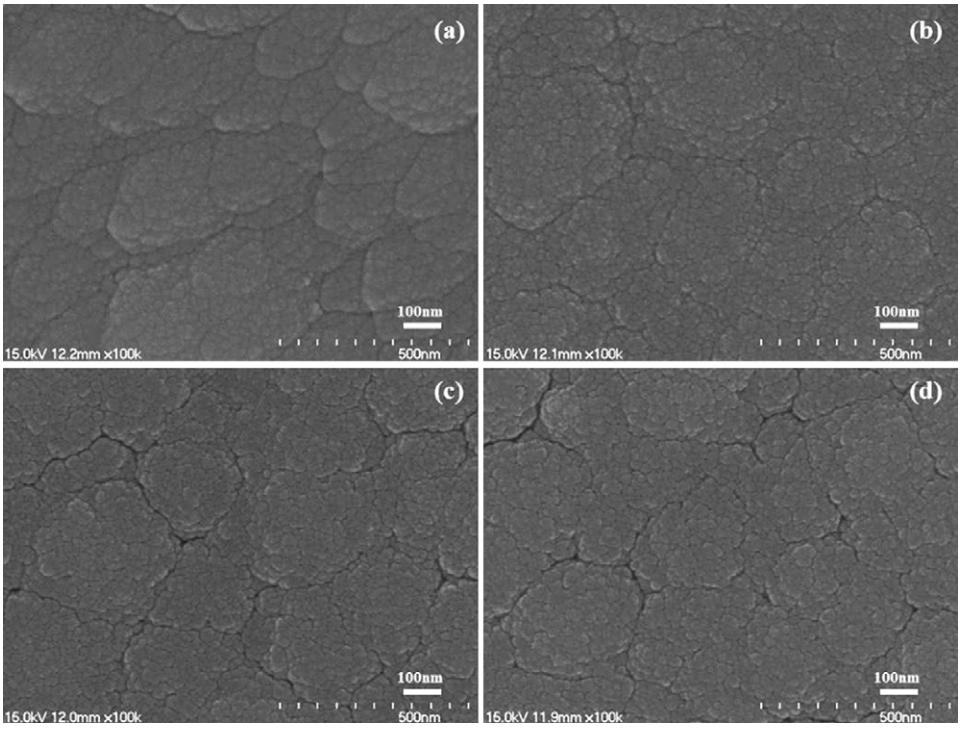

Fig. 2. FE-SEM images of the TiO_2 passivating layer deposited with various working pressures (a) 3 mTorr, (b) 5 mTorr, (c) 10 mTorr, and (d) 15 mTorr.

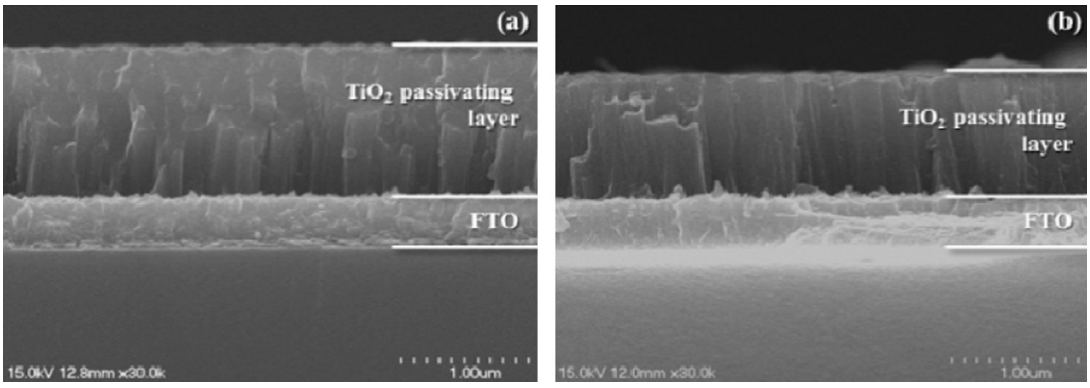

Fig. 3. Cross-sectional FE-SEM image of the TiO_2 passivating layer (a) 3 mTorr and (b) 10 mTorr.

rutile phase TiO_2 passivating layer. Fig. 3(b) presented SEM image of anatase phase TiO_2 passivating layer. The thickness of the TiO_2 passivating layer was measured at 1 μm. The cross-sectional view clearly indicates that it is comprised of three parts. The top part is the TiO_2 passivating layer 1 μm thick. The middle one is the FTO layer, and lowest one is the glass substrate.

Fig. 4 shows the transmission spectra of the FTO glass with the deposited TiO_2 passivating layers. Transmitted light passing through the TiO_2 thin film increases with an increasing wavelength. It is noted that the transmittance of the TiO_2 passivating layer prepared at 15 mTorr is higher than that of the TiO_2 passivating layer prepared at 3 mTorr in the visible range of 400–800 nm. The transmittance of the TiO_2 passivating layer is remarkably increased by the increase of the working pressure.

Fig. 5 shows the transmission spectra of the FTO glass with the deposited TiO_2 passivating layers with an increase in the sputtering time. The working pressure was fixed at 5 mTorr. The TiO_2 passivating layer sputtered for 1 h showed an identical transmittance at 75.74% at a 550 nm wavelength to that of the bare FTO glass sample. As the sputtering time increased, the optical transmittance decreased. Such a difference in scattering efficiency depending on light-scattering particle size and semitransparent layer film thickness might be related to the wavelength of the transmitted light [8].

The *I–V* characteristics of the prepared DSSCs, obtained under simulated sun light (an irradiated power density equal to $P_s = 100\ mW/cm^2$) are presented in Fig. 6. The DSSC prepared without a passivating layer had a short circuit current density (J_{sc}) of 7.68 A/cm^2, an open circuit potential (V_{oc}) of 0.68 V, and a cell conversion efficiency of 3.2%. It was found that crystalline structure of TiO_2 passivating layer influence the photocurrent density. The increase of J_{sc} is generally related to the enhancement of the number of photogenerated electrons which are efficiently transferred to TiO_2 electrode [9]. The DSSC fabricated with the TiO_2 passivating layer sputtered at 5 mTorr shows the highest efficiency (4.6%) value, due to the decreased conductivity for the electron transfer from the nanoporous TiO_2 layer to the FTO electrode. Table 1 summarizes the detailed performances of the fabricated DSSCs. It revealed that fill factors were lowered with the increasing of working pressure due to decreased optical transmittance. The fill factor was related to optical transmittance of TiO_2 passivating layer [10]. Fig. 7 shows the photocurrent–photovoltage characteristics of the solar cells with the TiO_2 passivating layer sputtered for 1 h, 3 h, and 5 h, respectively. The efficiency, fill factor, and the open circuit voltage for the solar cells are summarized in Table 2 The sputter-deposited blocking layers on the FTO improved the transmittance of the visible light, which was responsible for the increased photocurrent. Increase in thickness of the TiO_2

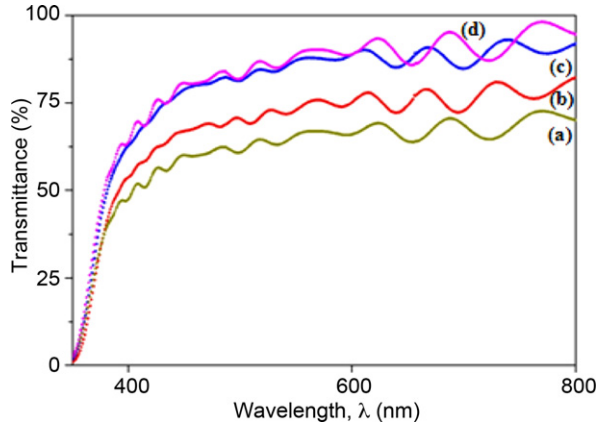

Fig. 4. Optical transmittance of the TiO_2 passivating layer with working pressures (a) 3 mTorr, (b) 5 mTorr, (c) 10 mTorr, and (d) 15 mTorr.

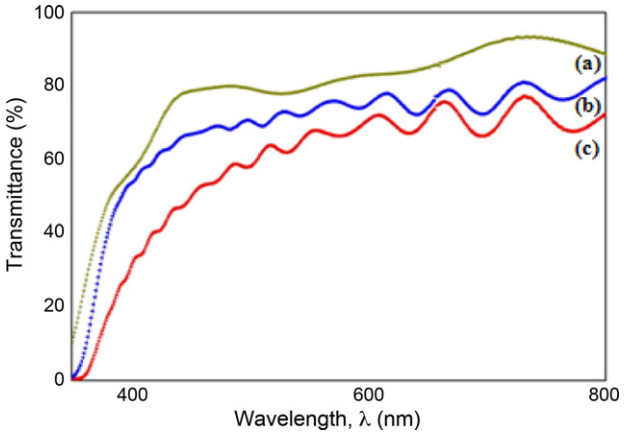

Fig. 5. Optical transmittance of the TiO_2 passivating layer with the sputtering time of (a) 1 h, (b) 3 h, and (c) 5 h.

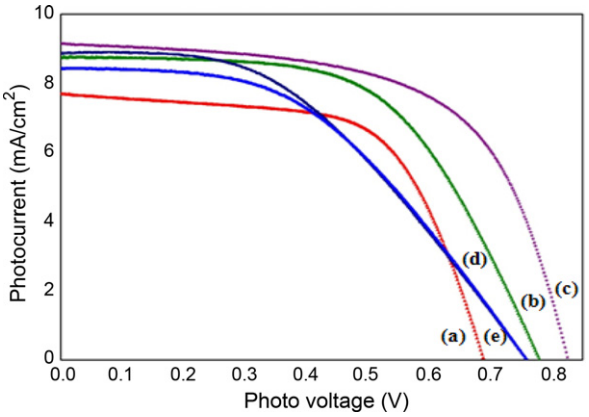

Fig. 6. Photocurrent and voltage curves of the DSSCs prepared with working pressures (a) without a passivating layer, (b) 3 mTorr, (c) 5 mTorr, (d) 10 mTorr, and (e) 15 mTorr.

Table 1
Photovoltaic performances of the DSSCs prepared with different working pressures.

	J_{sc} (A/m^2)	V_{oc} (V)	FF (%)	Efficiency (η)
(a) W/O passivation	7.68	0.68	62	3.2
(b) 3 mTorr	8.72	0.76	55	3.6
(c) 5 mTorr	9.14	0.82	61	4.6
(d) 10 mTorr	8.86	0.74	44	2.8
(e) 15 mTorr	8.41	0.74	42	2.6

Table 2
Photovoltaic performances of the DSSCs prepared with different sputtering times.

	J_{sc} (A/m^2)	V_{oc} (V)	FF (%)	Efficiency (η)
(a) 1 h	9.25	0.81	64	4.8
(b) 3 h	9.14	0.82	61	4.6
(c) 5 h	8.76	0.82	58	4.2

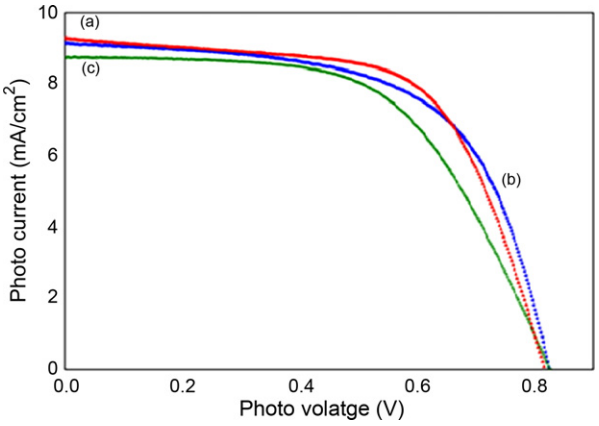

Fig. 7. . Photocurrent and voltage curves of the DSSCs prepared with sputtering times (a) 1 h, (b) 3 h, and (c) 5 h.

passivating layer resulted in decrease of efficiency (4.2%) due to decreased conductivity for electron transfer from nanoporous TiO_2 layer to the FTO electrode. Although the insertion of the TiO_2 passivating layer increases the efficiency by effective blocking of electron transfer from FTO to electrolyte, the decreased FF value demonstrated the decreased conductivity of the FTO electrode covered by TiO_2 passivating layer.

4. Conclusions

The properties of dye sensitized solar cells based on porous TiO_2 films deposited by RF magnetron sputtering have been studied. The rutile phase crystal property was found to be at its best at 0.5 mTorr. The TiO_2 passivating layers had more of the anatase phase with an increase of the working pressure. The thickness of the TiO_2 passivating layer deposited was 1 μm. The variation of the photoelectric conversion efficiency in the solar cells with different TiO_2 passivating layers is discussed, along with the analysis of the crystallite and optical properties of the films. The DSSC fabricated on a rutile phase TiO_2 passivating layer deposited FTO electrode shows the highest conversion efficiency of 4.6%, due to prevention of the electron transfer to the electrolyte. The photocurrent of the DSSC increased with an increased optical transmittance. It can be said that the improved photocurrent resulting from the passivating layer formation could be associated with the improved optical transmittance.

Acknowledgments

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