University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

2012

Effects of atomic layer deposited thin films on dye sensitized solar cell performance

Jonathan A. Campbell
University Of New South Wales

Mervyn deBorniol
ANSTO

Attila J. Mozer
University of Wollongong, attila@uow.edu.au

Peter J. Evans
Australian Nuclear Science And Technology Organisation

Robert P. Burford
University Of New South Wales

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Effects of atomic layer deposited thin films on dye sensitized solar cell performance

Abstract

"The application of thin titania films by atomic layer deposition on top of a low temperature nanoparticulate TiO₂ electrode was found to enhance the performance of dye sensitized solar cells. Dynamic measurements of photoinduced charge extraction showed that the atomic layer deposited top coat increased the electron lifetime at the same electron density. This was attributed to an increased electron trap concentration, which resulted in slower charge transport and increased charge carrier lifetimes.

Keywords

solar, cell, effects, performance, atomic, layer, deposited, thin, films, dye, sensitized

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Campbell, J. A., deBorniol, M., Mozer, A. J., Evans, P. J., Burford, R. P. & Triani, G. (2012). Effects of atomic layer deposited thin films on dye sensitized solar cell performance. *Journal of Vacuum Science and Technology Part A: International Journal Devoted to Vacuum, Surfaces, and Films*, 30 (1), 01A157-1-01A157-5.

Authors

Jonathan A. Campbell, Mervyn deBorniol, Attila J. Mozer, Peter J. Evans, Robert P. Burford, and Gerry Triani

Effects of atomic layer deposited thin films on dye sensitized solar cell performance

Jonathan A. Campbell

School of Chemical Sciences and Engineering, The University of NSW, Sydney, NSW 2052, Australia

Mervyn deBorniol

Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, NSW 2234, Australia

Attila J. Mozer

ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia

Peter J. Evans

Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, NSW 2234, Australia

Robert P. Burford

School of Chemical Sciences and Engineering, The University of NSW, Sydney, NSW 2052, Australia.

Gerry Triani^{a)}

Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights, NSW 2234, Australia

(Received 2 September 2011; accepted 8 November 2011; published 22 December 2011)

The application of thin titania films by atomic layer deposition on top of a low temperature nanoparticulate TiO₂ electrode was found to enhance the performance of dye sensitized solar cells. Dynamic measurements of photoinduced charge extraction showed that the atomic layer deposited top coat increased the electron lifetime at the same electron density. This was attributed to an increased electron trap concentration, which resulted in slower charge transport and increased charge carrier lifetimes. © 2012 American Vacuum Society. [DOI: 10.1116/1.3670397]

I. INTRODUCTION

Dye sensitized solar cells (DSSCs) are a promising photovoltaic technology capable of harvesting photons in an environmentally sustainable manner. These devices typically consist of a mesoporous semiconductor layer onto which a light harvesting dye is adsorbed. The generation of an electron and hole on illumination of the dye by photons creates a photocurrent in the porous TiO₂ layer and the cycle is closed by reducing the oxidized dye with the electrolyte. There are particular advantages of this technology, including the ability of cells to operate under low light intensity conditions and the low cost of manufacture.^{1–3}

To realize the full potential of low cost DSSCs, it is desirable to employ a high speed manufacturing process, such as reel to reel printing on polymeric materials. A typical DSSC requires sintering of the nanocrystalline TiO₂ particles at temperatures $\geq 400^\circ\text{C}$, which is too high for many heat sensitive substrates. Considerable research has been conducted into the use of low temperature titania nanoparticulate pastes^{4,5} in an effort to lower the processing temperature for DSSCs. However, there are several issues that remain unresolved when processing at temperatures below 200°C . These include the low mechanical strength of the titania films and the lack of nanoparticle connectivity, leading to high impedance in the cell.⁶

A number of methods for improving DSSC performance have been reported. These include the use of compact layers between the TiO₂ electrode and the underlying transparent conducting oxide film; treatment of the TiO₂ layer with TiCl₄ to improve particle connectivity; and coating the titania electrode with a thin film of an insulator such as Al₂O₃.^{7–11} Atomic layer deposition (ALD) has been used for the latter purpose in a number of recent studies.^{12,13} ALD is a surface mediated deposition process that allows film growth to be controlled on the nanoscale.¹⁴ A wide range of materials can be deposited by ALD, including metals, oxides, and polymers.¹⁵ The advantages of ALD when compared to other deposition techniques include the self-limiting film growth, separate dosing of reactants and control over the film chemistry. These characteristics lead to conformal coatings of high quality that are well suited to the treatment of porous materials such as the TiO₂ electrodes used in DSSCs.

Initial studies by our group on the effect of coating the TiO₂ nanoparticle electrodes of liquid DSSCs with thin TiO₂ films deposited by ALD found an enhancement in performance.¹⁶ The present study probes the basis for the observed enhancement through the use of a number of characterization tools. These are applied to matching pairs of samples prepared from a commercially sourced, low temperature paste. In each case, the ALD coating was applied to only one of each pair of samples. While ALD alumina has been the film material of choice in a number of studies,^{12,13} our current

^{a)}Electronic mail: gerry.triani@ansto.gov.au

work investigated, for the first time, the use of thin ALD TiO_2 films deposited at 120°C on TiO_2 nanoparticle electrodes prepared at low temperatures. This approach results in the deposition of a semiconducting amorphous film throughout the upper surface layer of the TiO_2 electrode that is expected to offer advantages over insulating alumina films.

II. EXPERIMENT

Anodes were prepared by coating cleaned FTO glass electrodes (Asahi 12 Ω/sq) with a low temperature titania paste (Peccell, PECC-01-06) by the doctor blading technique. The nanoparticle component of this paste had an average size of ~ 24 nm and a porosity of $\sim 63\%$. The resultant paste layer was approximately $5\text{ }\mu\text{m}$ thick, and was heated in air at 150°C for 5 min. The active area of the cells was $0.55\text{--}0.67\text{ cm}^2$. Thin films of titania were deposited onto the Peccell anodes by means of a flow-type hot-walled ALD reactor (ASM Microchemistry Model F-120). The chamber was continually flushed with nitrogen gas flowing at 550 sccm, and pressure was maintained at less than 1 mbar. The titanium tetrachloride (TiCl_4) and water precursors were delivered from Peltier cooled reservoirs maintained at 20°C . A pulsing sequence of 0.5 s exposure to TiCl_4 followed by a 1.0 s purge, then 1.0 s exposure to water followed by a 1.5 s purge was used. All coatings were deposited using 50 cycles at 120°C , which produced a coating thickness of ~ 3 nm. While 50 cycles was adopted for the present study, a number of tests were also performed on cells coated with 25 and 75 cycle films. These showed comparable (75 cycles) or negligible (25 cycles) improvement. After processing, electrodes were placed into a 0.3 mM solution of N719 dye (Solaronix) for 24 h. The cells were then assembled by placing a $25\text{ }\mu\text{m}$ Surlyn spacer (Solaronix) between the anode and a sputtered Pt counterelectrode. LiI based electrolyte solution was then vacuum filled between the electrodes.

Both the ALD coated and control cells were tested using a 1000 W solar simulator equipped with an AM 1.5 G filter (Newspec Ltd.). The light intensity was adjusted to 100 mW cm^{-2} using a calibrated Si photodetector (Peccell Technologies Inc., PECSI01). A black mask with an open area of 0.81 cm^2 was attached to the FTO glass facing the solar simulator. The current–voltage curves were recorded using a source-meter (Keithley Instruments, Model 2400) controlled by a custom-made LABVIEW program. The voltage was swept from 850 to -30 mV in 5 mV steps. Stepped light-induced transient measurements of photocurrent and voltage (SLIM-PCV) were also performed on the entire area of the DSSCs using illumination from a continuous laser (Coherent Lab-laser, $\lambda = 635$ nm). A small portion of the laser intensity was stepped down and the induced current transients at short circuit, and voltage transients at open circuit were recorded with a fast multimeter (Advantest, AD7461 A). The transients were fitted with a single exponential function whereupon the electron diffusion coefficient (D) and electron lifetime (τ) were determined. The electron densities at identical laser illumination intensities were determined by a charge extraction method^{17,18} in which devices are

illuminated and held at open circuit with a potentiostat before the light intensity is switched off at the same time the DSSC is switched from open to short circuit. The extracted current was integrated with the electron density calculated from the amount of charge extracted and the geometric dimensions of the TiO_2 film. The porosity of the electrode was not taken into account in calculating the electron density. The incident photon-to-electron conversion efficiency (IPCE) of samples was measured by means of an Xe lamp/monochromator setup. The current response of the cell with zero applied external bias was determined as a function of wavelength in the range 300–850 nm. The IPCE was calculated with reference to a calibrated silicon photovoltaic cell.

Following performance testing, the cells were dismantled for SIMS and dye desorption analysis. Following removal of the counterelectrode, the photoanodes were rapidly flushed with acetonitrile several times to remove electrolyte and dried with nitrogen. Elemental depth profiling of the photoanodes was performed on a dynamic SIMS instrument (Cameca ims 5f). For this purpose, a Cs^+ primary ion beam was rastered over a $250 \times 250\text{ }\mu\text{m}^2$ area and secondary cesium cluster ions (MCs^+) from a $\sim 55\text{ }\mu\text{m}$ central region were detected. Subsequently, the amount of N719 dye incorporated in the TiO_2 photoanodes was determined by immersing them in 4 ml of 0.1 M NaOH and measuring the solution absorbance using an ultraviolet–visible spectrometer (PerkinElmer Lambda 35).

III. RESULTS AND DISCUSSION

The results of applying a thin amorphous TiO_2 layer to previously formed nanoparticle TiO_2 nanoparticle electrodes are presented in Fig. 1 and Table I. In each case, the control and coated pairs of samples were selected from the same batch. The improvements in efficiency were in the range 10%–25%, which were mostly due to increases in J_{sc} . Similar efficiency enhancements have been observed for a large number of test DSSCs in which the TiO_2 electrodes were

FIG. 1. (Color) Current–voltage curves for cells used in this study.

TABLE I. Performance and dye absorption data for ALD coated and control cells.

Sample number	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	FF	Eff (%)	Dye concentration (mol/cm ⁻²) ^a
144 coated	8.17	780	0.70	4.47	8.5×10^{-8}
145 control	6.99	775	0.71	3.82	8.0×10^{-8}
157 coated	8.43	795	0.71	4.78	8.0×10^{-8}
158 control	6.64	780	0.72	3.72	8.5×10^{-8}

^aNormalized to area of photoanode.

coated by ALD. Some of these results have been reported elsewhere.¹⁶

The effect of amorphous TiO₂ thin films on electrode composition was investigated by means of SIMS analysis on the dye impregnated photoanodes from dismantled devices. The Cl and Ru profiles for the coated (144) and control (145) samples are shown in Fig. 2. Significant differences in these elements are apparent at sputter times between 0 and 600 s. The depth extent of these differences was estimated by profilometry to be $\sim 1 \mu\text{m}$. In this region, increased chlorine was detected in the sample with the low temperature TiO₂ ALD coating.¹⁹ This element, which was present at ~ 1.5 at. %, provided a qualitative marker of the depth to which the ALD film had penetrated the porous TiO₂ electrode. The ALD coated region also exhibited a decrease in the amount of Ru relative to the constant signal at times >600 s, which indicated less dye was present in the volume coated with ALD

FIG. 2. (Color) SIMS depth profiles for ALD coated (a) and uncoated (b) TiO₂ nanoparticle photoanodes.

FIG. 3. (Color online) Dependence of electron lifetime on electron density for ALD coated (144 and 157) and uncoated (145 and 158) test cells.

titania. This effect was attributed to the decrease in average diameter of the coated pores, which in turn reduced the surface area available for dye absorption. In the present study, the thin ALD coating did not affect the total amount of dye absorbed in the photoanode (refer to Table I). However, thicker coatings will eventually lead to closure of the surface pores that will ultimately prevent dye absorption.

The concentrations of N719 desorbed from the cells are listed in Table I. No systematic or significant differences in dye concentrations were observed despite the reduction in Ru detected in the coated samples. Thus, it seems unlikely that the improvements in performance shown in Table I are due to the amount of dye absorbed by the photoanodes.

The diffusion coefficient and electron lifetime versus the short circuit current density (J_{sc}) and electron density, respectively, are shown in Fig. 3. The decreasing electron lifetimes with increasing electron densities (light intensity) are attributed to filling of electron traps with photoinjected electrons.^{20–22} The ALD top coating improves the electron

FIG. 4. (Color online) Dependence of electron diffusion coefficient on J_{sc} for ALD coated (144 and 157) and uncoated (145 and 158) test cells.

lifetime at the same electron density by almost an order of magnitude, which suggests a slower recombination rate between the photoinjected electrons in the TiO_2 and the acceptor species in the electrolyte (I_3^-).

Furthermore, the electron diffusion coefficients at matching short circuit current densities in Fig. 4 were observed to decrease following ALD deposition, which suggests that the increased concentration of electron traps in the amorphous TiO_2 ALD layer may be responsible for slower charge transport and increased charge carrier lifetime. The open circuit voltage at the same electron density was also decreased as shown in Fig. 5. This effect is attributed to a negative shift of the conduction band (CB) potential of the TiO_2 film following the ALD top coat. The open circuit voltage (V_{oc}) of DSSCs is proportional to the electron density in the TiO_2 under illumination and in the dark. A higher V_{oc} at matching electron density is typically interpreted as a shift in the conduction band potential^{23,24} as observed here. At the same time, the electron density at V_{oc} has increased due to the longer electron lifetime and higher J_{sc} , so the V_{oc} under AM 1.5 illumination did not change significantly. The increase in J_{sc} following ALD top coat is thought to originate from improved injection from photoexcited N719 into the TiO_2 . A negative shift in the CB potential has been observed, which increases the driving force for charge injection. Injection kinetic studies, beyond the scope of this communication, are required to determine the possible increase in injection efficiency following ALD TiO_2 deposition.

Figure 6 displays plots of IPCE as a function of wavelength for the cells listed in Table I. At the maximum value of 530 nm, the IPCE of the ALD coated photoanodes is significantly higher than that of the uncoated controls. As the IPCE is the ratio of the number of charge carriers collected to the number of photons impinging on the solar cell, these results suggest that the generation and collection of electrons is more efficient in the ALD coated photoanodes, which is reflected in higher J_{sc} .

Fig. 5. (Color online) Dependence of V_{oc} on electron density for ALD coated (144 and 157) and uncoated (145 and 158) test cells.

Fig. 6. (Color online) IPCE spectra of cells with ALD coated and uncoated TiO_2 photoanodes.

IV. SUMMARY AND CONCLUSIONS

Atomic layer TiO_2 thin films deposited on DSSCs prepared from a low temperature paste have been shown to improve their performance. The deposition conditions utilized in the present work produced a film that penetrated to a depth of $\sim 1 \mu\text{m}$ into the porous photoanode. This approach significantly reduced the processing time compared with that required to coat fully the entire TiO_2 nanoparticle electrode. The addition of an amorphous TiO_2 layer on the upper surface of the photoanode resulted in an improvement to J_{sc} and hence the efficiency of the cell. An improvement in electron lifetimes showed the interfacial layer acted to suppress electron recombination. Thus the application of ALD films to low temperature DSSCs shows potential as an enabling technology platform to bridge the gap between performance and process temperature limitations.

ACKNOWLEDGMENT

The financial support of the Cooperative Research Centre for Polymers III is acknowledged.

- ¹B. O'Regan and M. Grätzel, *Nature (London)* **353**, 737 (1991).
- ²M. Grätzel, *J. Photochem. Photobiol. C*, **4**, 145 (2003).
- ³T. Miyasaka, M. Ikegami, and Y. Kijitori, *J. Electrochem. Soc.* **154**, A455 (2007).
- ⁴D. Zhang, T. Yoshida, T. Oekermann, K. Furuta, and H. Minoura, *Adv. Funct. Mater.* **16**, 1228 (2006).
- ⁵T. Yamaguchi, N. Tobe, D. Matsumoto, and H. Arakawa, *Chem. Commun. (Cambridge)* **45**, 4767 (2007).
- ⁶A. Ofir, S. Dor, L. Grinis, A. Zaban, T. Dittrich, and J. Bisquert, *J. Chem. Phys.* **128**, 064703 (2008).
- ⁷H. Lin, X. Li, Y. Liu, and Y. Li, *Mater. Sci. Eng. B* **161**, 2 (2009).
- ⁸J. Xia, N. Masaki, K. Jiang, and S. Yanagida, *Chem. Commun.* **2**, 138 (2007).
- ⁹A. Burke, S. Ito, H. Snaith, U. Bach, J. Kwiakowski, and M. Grätzel, *Nano Lett.* **8**, 977 (2008).
- ¹⁰P. Sommeling, B. O'Regan, R. Haswell, P. Smit, N. Bakker, J. Smits, J. Kroon, and J. van Roosmalen, *J. Phys. Chem. B* **110**, 19191 (2006).
- ¹¹J.-Y. Kim, S. Lee, J.-H. Noh, H.-S. Jung, and K.-S. Hong, *J. Electroceram.* **23**, 422 (2009).
- ¹²C. Lin, F.-Y. Tsai, M.-H. Lee, C.-H. Lee, T.-C. Tien, L.-P. Wang, and S.-Y. Tsai, *J. Mater. Chem.* **19**, 2999 (2009).
- ¹³V. Ganapathy, B. Karunakaran, and S.-W. Rhee, *J. Power Sources* **195**, 5138 (2010).
- ¹⁴M. Ritala and M. Leskela, in *Handbook of Thin Film Materials*, edited by N. S. Nalwa (Academic, San Diego, 2002), Vol. 1, pp. 103–159.

- ¹⁵S. George, *Chem. Rev.* **110**, 111 (2010).
- ¹⁶G. Triani, J. A. Campbell, G. Moad, G. E. Collis, P. J. Evans, R. P. Burford, and A. J. Moser, Solar Cell and Method for Preparation Thereof, WO 2009/013285 A1, (29 January 2009).
- ¹⁷N. W. Duffy, L. M. Peter, R. M. G. Rajapakse, and K. G. U. Wijayantha, *Electrochem. Commun.* **2**, 658 (2000).
- ¹⁸S. Nakade, T. Kanzaki, W. Kubo, T. Kitamura, Y. Wada, and S. Yanagida, *J. Phys. Chem. B* **109**, 3480 (2005).
- ¹⁹G. Triani, J. A. Campbell, P. J. Evans, J. Davis, B. A. Latella, and R. P. Burford, *Thin Solid Films* **518**, 3182 (2010).
- ²⁰N. Kopidakis, K. D. Benkstein, J. van de Lagemaat, and A. J. Frank, *J. Phys. Chem. B* **107**, 11307 (2003).
- ²¹J. Nelson, *Phys. Rev. B* **59**, 15374 (1999).
- ²²K. Wagner, M. J. Griffith, M. James, A. J. Moser, P. Wagner, G. Triani, D. L. Officer, and G. G. Wallace, *J. Phys. Chem. C* **115**, 317 (2011).
- ²³A. Allegrucci, N. A. Lewcenko, A. J. Moser, L. Dennany, P. Wagner, D. L. Officer, K. Sunahara, S. Mori, and L. Spiccia, *Energy Environ. Sci.* **2**, 1069 (2009).
- ²⁴A. J. Moser, P. Wagner, D. L. Officer, G. G. Wallace, W. M. Campbell, M. Miyashita, K. Sunahara, and S. Mori, *Chem. Commun.* **39**, 4741 (2008).

Copyright of Journal of Vacuum Science & Technology: Part A is the property of AVS, The Science & Technology Society and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.