Surface & Coatings Technology 276 (2015) 116–120

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Dye adsorption on atomic layer deposited aluminum oxides for tin-oxide-based dye sensitized solar cells

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ARTICLE INFO

Article history:
Received 4 October 2013
Revised 29 May 2015
Accepted in revised form 25 June 2015
Available online 2 July 2015

Keywords:
SnO_2 photoelectrodes
ALD
Alumina oxide
Dye absorption

ABSTRACT

In this paper, the mesoporous SnO_2 photoelectrodes were coated by ultra-thin alumina through atomic layer deposition (ALD) technique to improve the solar cell efficiency. We find that an ultra-thin Al_2O_3 coated on mesoporous SnO_2 photoelectrodes can improve the open-circuit voltage, short-circuit current, and fill factor, leading to the increase of the energy conversion efficiency. After the measurement by ultraviolet spectrometer in detail we conclude that the enhanced adsorption of the dye N719 after the aluminum oxide coating SnO_2 is one of the main reasons to promote the cell efficiency.

1. Introduction

To date, semiconductor solar cells dominate commercial markets with crystalline Si over 80% share [1]. Dye-sensitized solar cells (DSSCs), however, as one of the new generation solar cells attracts tremendous attention because of its sample structure, easy handling, cheap raw materials, low manufacturing cost, and so on [2]. In order to make DSSCs more competitive with commercial energy production technologies, lots of researches have been extensively carried out to increase their conversion efficiency. For instance, TiO_2 electrodes were treated by O_2 plasma to reduce trap states [3], blocking layers were prepared on fluorine-doped tin oxide (FTO) [4], and the high band-gap semiconductor metal oxides like ZnO [5] or the metal oxides such as MgO [6] and Al_2O_3 [7] were inserted between the porous metal oxide film and the dye to reduce their interface recombination. In particular, the metal oxide layer, which was carried out by various techniques [8–10], mainly relied on the sol–gel process. In the sol–gel process, however, a higher temperature treatment is indispensable, which put many limitations on the process for DSSCs, especially for flexible substrate DSSCs [11]. As an alternative method, atomic layer deposition (ALD), which can offer an atomic level control of the chemical composition and the thickness at low temperature (down to 33 °C for Al_2O_3) [12], is then preferred for consideration. Additionally, compared with the sol–gel process, ALD can offer a highly conformal coating that is very important for nanoporous structures, especially for the modification of the mesoporous photoelectrode in DSSCs. It is believed that ALD is an ideal method to deposit nano-scale metal oxides on nanoporous structural photoelectrode for DSSCs.

Although there have been quite a few large-band-gap semiconductors used as the photoelectrodes for dye-sensitized solar cells, the highest energy conversion efficiency was still achieved by titanium dioxide (TiO_2) photoelectrodes. However, the electron transport speed in TiO_2 particles is relatively slow, and the system also requires a slow redox shuttle, usually I^-/I_3^-. It significantly limits the light conversion efficiency of dye-sensitized solar cells. Therefore other semiconductors with higher electron mobility, such as SnO_2, are expected to replace TiO_2 for fast electron transport.

SnO_2 demonstrates a higher mobility and has a larger band gap (3.6 eV) than TiO_2 (3.2 eV) [13], which will create fewer oxidative holes in the valence band, which is beneficial for long-term stability of DSSCs. But, SnO_2-based DSSCs could only generate a lower energy conversion efficiency, which is attributed to the fast interfacial electron recombination and the low isoelectric point (IEP, SnO_2 IEP is at pH 4–5 whereas TiO_2 IEP is at pH 6–7). A lower IEP causes less adsorption amount of the dye [14].

Modified SnO_2 surface to retard the electron recombination is regarded to be much efficient approach. J. T. Hupp and Prasittichai [15] exploited the Al_2O_3-coated SnO_2 photoanode for DSSCs with the I^{3-}/I^- couple as the redox electrolyte. They obtained a five-fold increase of cell efficiency after a single cycle of ALD Al_2O_3 coating SnO_2, because the monolayer Al_2O_3 increased the lifetime of injected electrons and led to the high conversion efficiency.

In this paper, we also used SnO_2 as photoelectrode for DSSCs with the I^-/I_3^- redox couple. Our work focused on the improvement of the

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http://dx.doi.org/10.1016/j.surfcoat.2015.06.057
0257-8972/

dye adsorption with the ALD Al_2O_3 coating on mesoporous SnO_2 photoelectrode. The correlation of the ALD process parameters with the dye adsorption and cell efficiency is emphasized.

2. Experiments

Photoelectrodes were prepared on 15 Ω cm^{-2} FTO-coated glass (Nippon Sheet Glass—NSG). The FTOs were cleaned ultrasonically in detergent solution for 10 min, following by cleaning in KOH (Tianjin Chem. Co., China; chemical pure), ethanol and de-ionized water for 10 min, respectively, then dried with the nitrogen stream. The SnO_2 layer was prepared by the process of doctor blading a paste of SnO_2 (Alfa Aesar, NanoArc®, 13–19 nm APS Powder, S.A. 45–65 m^2/g) on the FTO surface, and then annealing in air at 450 °C for 30 min. The thicknesses of the SnO_2 layers were approximately 12 μm after repeating this process for four times. It is worth noting that there was no dense layer of SnO_2 on FTO coated-glass as previous done [15]. ALD Al_2O_3 was carried out in a home-made ALD system, which was performed at 150 °C with trimethylaluminum (TMA) (Jiangsu Nata Opto-electronic Material Co., Ltd, China, 98%) as a metal precursor and water as oxidant. One cycle of close-mode ALD consisted of the following steps: dose TMA, isolate the chamber, and N_2 purge; then dose H_2O, isolate the chamber, and N_2 purge. The period of each step was varied to explore their influence on the dye adsorption and DSSC properties. The thickness of Al_2O_3 was measured by spectroscopic ellipsometry, and the growth rate per cycle was then calculated based on the linear fitting of ALD Al_2O_3 thickness at 50, 100 and 300 cycles on silicon substrates. The obtained growth rate was ~0.12 nm/ cycle, which was consistent with the data reported in other works [16–18].

For the detection of the dye adsorption, the SnO_2 photoelectrodes with and without the ALD Al_2O_3 coatings were immersed in dye cis-di (thiocyanato)-N,N-bis (2,2′-bipyridyl-4,4′-dicarboxylic acid)-ruthenium(II) (noted as N719 dye) for 24 h, where iodide based electrolyte was used as a redox couple. After taken out from the liquid, the dye loaded electrodes were rinsed with ethanol for several times to remove the excess adsorptive dye, and then dried by a nitrogen stream prior to the ultraviolet measurement. The adsorption spectra were recorded with a Shimadzu UV-2501PC UV–vis spectrometer.

Electrochemical impedance spectroscopy (EIS) measurement was carried out in the frequency range of 100 mHz to 100 kHz at 0.45 V with a potential pulse of 10 mV in amplitude to analyze the interface resistance in cells. Surface morphology and microstructure of the coating layer were examined by field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM), respectively. The photocurrent-density-to-voltage (J–V) characteristic curves was measured by Keithley 4200 under a AM 1.5 solar simulator (100 mW/cm^2 xenon lamp).

3. Results and discussion

We firstly exploited the role of ALD Al_2O_3 coatings on the cell efficiency. The primary process parameters of one cycle close-mode ALD Al_2O_3 was the following: dose TMA for 1 s, isolate the whole chamber for 1 s, and N_2 purge for 15 s; then dose H_2O for 1 s, isolate the whole chamber for 1 s, N_2 purge for 15 s, which is denoted as 1-15-1-15. The SnO_2 photoelectrodes were then modified by coating with one, two, and three cycles of ALD alumina, respectively.

Fig. 1(a) shows the comparison of the J–V characteristics of two kinds of cells with and without ALD Al_2O_3 interlayer under AM 1.5 solar simulator, and Table 1 summarizes the derived results. For the pristine sample, the efficiency was 1.04% in bare SnO_2 photoelectrode, but after the ultra thin Al_2O_3 coating, the maximum conversion efficiency reached 1.6%, i.e. increased by ca. 54% in average of 10 samples (ca. ±4% deviation). Both of the open-circuit voltage (V_{oc}) and the short-circuit current (J_{sc}) remarkably increased in this sample. A closer investigation of Fig. 1(a) and Table 1, we found that the improvement of the cell efficiency depended on the ALD cycles. The highest cell efficiency of 1.6% was obtained in two cycles of ALD Al_2O_3 modified one.

As the cycle number of ALD Al_2O_3 was increased to 3, the efficiency was slightly lower than that for the one with 2 cycles of ALD Al_2O_3 modification, even though the J_{sc} was the highest in all samples. When the Al_2O_3 was deposited for 15 cycles, the efficiency was still higher than the control one but the short-circuit current was very low.

We then investigated the process parameters of ALD Al_2O_3 on the cell efficiency. We extended the period of N_2 purge from 15 s to 30 s, and varied the dosing times for TMA and H_2O from 1 s to 10 s, respectively. The extension of N_2 purge period from 15 s to 30 s aimed to avoid chemical vapor deposition in the process; while the extension of precursor dosing time was for achieving the conformal coating of Al_2O_3 on the mesoporous SnO_2. Fig. 1(b) shows the J–V characteristics of these DSSCs and the obtained cell parameters are also listed in Table 1. The highest efficiency reached 2.01%, ca. 94.2% increase on average for 10 samples (ca. ±4% deviation) with the modification of ALD Al_2O_3. The highest cell efficiency of 2.01% was also attained for two cycles of ALD Al_2O_3 modification. The open-circuit voltage (V_{oc}) was greatly increased in this sample.

The cell efficiency continuously increased with the first 3 cycles of ALD Al_2O_3 modification, even though the increasing rate was relatively small. However, when the ALD Al_2O_3 was processed for 15 cycles, the efficiency was lower than the pristine one, 27% decrease after the Al_2O_3 coating as shown in Table 1.

The highest efficiency always appeared for the samples with two cycles of ALD Al_2O_3 modification, which confirms the assumption of suppressed interfacial charge recombination by the ultrathin layer on SnO_2 surface; and the results appeared in two cycles of ALD Al_2O_3 can be reasoned based on the ALD principle: where one cycle deposition

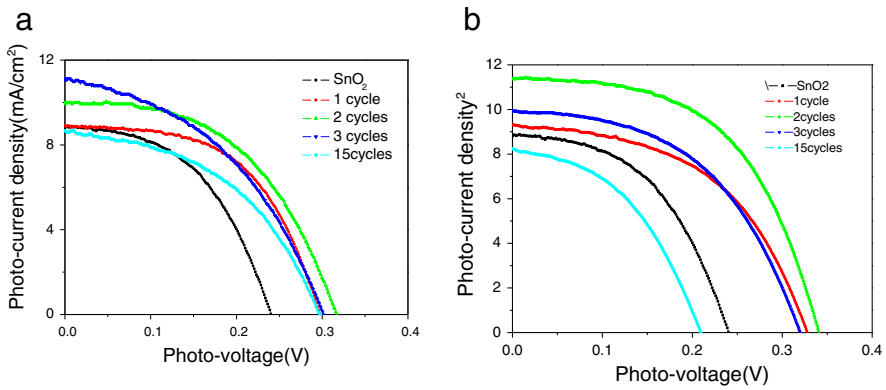

Fig. 1. J–V characteristics of SnO_2 coated by ALD alumina versus the ALD processing parameters and cycles (a—1-15-1-15; b—10-30-10-30).