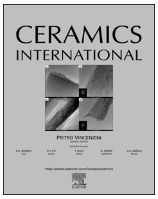
Ceramics International 42 (2016) 11989–11997

Contents lists available at ScienceDirect

Ceramics International

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



Solution processing of TiO_2 compact layers for 3rd generation photovoltaics

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ARTICLE INFO

Article history:
Received 22 January 2016
Received in revised form
31 March 2016
Accepted 22 April 2016
Available online 23 April 2016

Keywords:
TiO_2 compact layer
Solution processing
Near-infrared sintering
3rd Generation photovoltaics

ABSTRACT

In this study, we introduce a new method for the deposition of TiO_2 compact layers which involves the deposition of a wet film of an inorganic titanium (IV) precursor followed by fast hydrolytic conversion to crystalline TiO_2 under near infrared radiative (NIR) treatment. With this, we aim to provide a scalable alternative to methods conventionally employed in laboratories for the fabrication of 3rd generation photovoltaic devices, such as high temperature pyrolysis or spin coating of organic titanium (IV) precursors. Optimization of our solution process is presented in detail. Structural features and crystalline properties of solution processed compact layers are characterized by FEG-SEM imaging and x-ray diffraction analyses and compared to compact layers produced by conventional laboratory techniques. Minimization of electron recombination is evaluated in standard liquid I^-/I_3^- dye-sensitized solar cells (DSC). The results show that a compact, homogenous, high coverage yield crystalline TiO_2 anatase layer can be produced by sequential deposition of 2–3 solution processed titanium oxide layers, each in under 30 s. In standard liquid I^-/I_3^- DSC the solution processed compact layers strongly increased the electron lifetime, τ_n, when compared to cells prepared on a bare FTO substrate.

1. Introduction

The fabrication of dye-sensitized solar cells (DSC) and more recent technologies such as lead-halide perovskite solar cells usually involves the deposition of a very thin (50–150 nm) and compact layer of TiO_2 at the surface of the photo-electrode substrate. This layer ensures the transfer of electrons photo-generated by the dye-sensitized mesoporous oxide or lead-halide perovskite layer to the transparent conductive oxide (TCO) of the substrate while minimizing the occurrence of short-circuits generated by electron recombination, a phenomenon also referred to as shunting [1–15]. In I^-/I_3^- based liquid dye-sensitized solar cells, the recombination of electrons at the substrate is a relatively slow process, hence the application of a TiO_2 blocking layer is known to moderately improve device performance. However, the presence of this layer is critical to the performance of liquid devices using the Co(III)/Co(II) electrolyte systems [16] and solid-state DSCs [2–5]. In these systems the electron recombination occurring at the interface between the TCO/hole transporter is approximately two orders of magnitude faster than in I^-/I_3^- liquid-based DSCs, hence the blocking layer plays a critical role in the fabrication of functional devices. In the case of lead-halide perovskite solar cells, the TiO_2 blocking layer acts as an n-type contact and minimizes electron back transfers from the FTO surface which allows the fabrication of high voltage devices. A number of titania deposition methods have been suggested such as spin coating, atomic layer deposition, sputtering, etc. [12–15]. A few research groups have reported on the fabrication of blocking layer-free lead-halide perovskite solar cells [17], however the majority of high performance devices contain an inorganic or organic electron collection layer.

The TiO_2 blocking layer is usually produced with a thickness in the range 50–150 nm, depending on the type of 3rd generation PV technology and on the fabrication method. The thickness is ultimately optimized to minimize resistive losses [4,15] while ensuring enough material has been deposited to provide a high coverage yield over the substrate. The TiO_2 blocking layer is conventionally deposited using a multi-cycle spray pyrolysis technique [1,2,4,18]. A liquid organic titanium precursor, such as titanium diisopropoxide bis(acetylacetonate) (TAA), is sprayed over the conductive side of a TCO-glass substrate maintained at high temperature (up to 450 °C) on a hotplate. The build-up of a

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http://dx.doi.org/10.1016/j.ceramint.2016.04.125
0272-8842/

50–150 nm compact layer requires the application of a large number of spray cycles, each of them separated by a time interval of approximately 10 s allowing solvent evaporation and crystallization of the TiO_2. Although widely employed in laboratories, this method presents a number of technical difficulties, in particular low reproducibility associated to the manual aspect of the operation, and safety hazards associated to the spraying of flammable solvents over high temperature surfaces. Finally, the multi-step time consuming nature of the operation makes it particularly unsuited to large scale manufacturing of DSC or perovskite devices. Other methods are currently under development such as spin coating [19,20] which have been designed for the fast deposition of thicker TiO_2 compact layers, up to 225 nm [15]. Here again, this laboratory technique is relatively well suited and reproducible for substrates of small dimensions $<2\times2$ cm^2, but cannot be transferred to roll-to-roll manufacturing and presents real technical challenges when applied to larger substrates. Another more recent approach consists of using atomic layer deposition (ALD) of very thin TiO_2 layers, especially in the case of halide perovskite devices where 2 nm of material is sufficient to prevent electron recombination effectively [13]. However, this technology is associated with high production costs due to the very slow deposition rates of material and vacuum nature of the process.

In order to address the large-scale process bottlenecks associated with conventional deposition of TiO_2 compact layers, a new method was developed in our laboratories: a solution of titanium (IV) chloride tetrahydrofurane ($TiCl_4\cdot THF$) prepared in a mixed water/isopropanol solvent was coated, dried and hydrolyzed into a thin layer of crystalline TiO_2; the conversion of the precursor was induced by a fast heating of the FTO-glass substrate in under 0.5 min using near infrared (NIR) radiation under atmospheric pressure conditions [21]. The application of NIR radiation has already proven successful for a number of applications, namely (i) for the sintering of TiO_2 mesoporous films [22], (ii) the platinization of TCO-glass counter electrodes [23] and (iii) the curing of silver inks [24]. The main advantage of this NIR radiative method relates to the very short, roll-to-roll compatible processing time (<30 s) required for the full conversion of the precursor solution into crystalline TiO_2 compared to the 30 mins oven/hotplate sintering step conventionally used in laboratories. This is largely facilitated because of the chemical nature of the precursor: unlike organo-Ti precursors, aqueous $TiCl_4$ can be converted into crystalline TiO_2 anatase at low temperature (80 °C, P_{atm}), as demonstrated in previous work [25]. Another benefit associated with the use of this precursor resides in its aqueous nature, which makes it much less susceptible to self-ignition, an important factor to consider in the scale-up of operations. Finally, the dynamics of the method described in this work, where the sample is irradiated while in motion on a small conveyor belt system, should enable a straight forward transition towards continuous roll-to-roll manufacturing. It is anticipated that the solution process described in this work, once automated, is easily applicable to the fabrication of large devices built on TCO-glass and further transferable to roll-to-roll processable substrates such as metal coils.

This work compares structural properties of sprayed vs. solution processed blocking layers. Emphasis is given to the effect of process parameters, for instance the number of sprays, concentration of the $TiCl_4$ precursor and impact of solvent modifications. The technological steps involved in the development and optimization of our solution deposition method are thoroughly explained and supported by optical microscope observations and wetting angle measurements. The morphological and crystalline properties of high temperature sprayed vs. solution processed blocking layers are further characterized using extensive electron imaging (FEG-SEM) and X-ray diffraction analyses. Finally, standard non-optimized I^-/I^{3-}-based liquid DSC devices were fabricated to probe the performance of solution processed TiO_2 blocking layers in minimizing electron recombination. This photovoltaic system was selected because the effect of pin-holes is much easier to observe when a substrate is put in contact with small ions in solution and has already been very well characterized in previous work [6–8]. Photovoltage decay measurements and I/V data were collected from devices built on solution processed and optimized sprayed TiO_2 blocking layers and electron lifetime plots were produced to compare the effectiveness of the different types of blocking layers.

2. Experimental

2.1. Preparation of TiO_2 blocking layers

2.1.1. Spray pyrolysis

A solution of 0.2 M titanium di-isopropoxide bis(acetylacetonate) (or TAA) in ethanol was manually sprayed with an art spray gun (Sealey, Model No. AB932) over the conductive surface of a fluorine-doped tin oxide (FTO)-coated glass, according to the method developed by Kavan et al. [1]. The substrate was pre-heated and maintained at 450 °C on a hotplate. A series of 1–50 sprays were applied successively at 10 s intervals. One edge of the substrates was masked using a thin glass slide in order to create a clean step at the edge of the blocking layer, used to measure the thickness of material deposited.

2.1.2. Spin coating

A 240 mM solution of Ti tetraisopropoxide (99.99%, Sigma Aldrich) was prepared in ethanol with additional 7 µL/ml of 2 M HCl and filtered using 0.45 µm pore size filters. A total volume of 200 µL was dispensed over a 7.84 cm^2 TCO-coated glass substrate. Spin coating was carried out using 1 cycle at 500 rpm for 10 s, immediately followed by a second cycle at 2000 rpm for 60 s. The wet film was dried in an oven at 150 °C for 10 mins and sintered on a pre-heated hotplate at 450 °C for 30 min.

2.1.3. Solution processing

The precursor solution was prepared by dissolving titanium(IV) chloride tetrahydrofurane complex ($TiCl_4\cdot THF$, $\geq$97.0 purum from Sigma Aldrich) in distilled water at a concentration of 10–30 g/L. Alternately, a mixed solvent of isopropanol (IPA) and distilled water at 30/70 v/v was employed, the addition of isopropanol aiming to improve the wetting properties of the precursor on the FTO-coated substrate. The precursor solution was spread across the surface of the substrate by doctor blading, at T_{amb}. The coated substrate was immediately transferred to the sample platform of the NIR oven and heat treated consecutively at 30% and 80% radiation power, over a total duration of 25 s The NIR equipment used in this work (Adphos NIR/IR Coil lab LV2) was described in detail in previous work [21]. The wetting properties of the precursor solution were investigated using an FTA 1000 B Class (First Ten Angstrom, USA) dynamic contact angle measurements apparatus. The data were computed from a series of snap shots of a single droplet released from the tip of a syringe onto the surface of a TEC 15 substrate using a high speed camera (up to 250 frames/s). Evolution of the shape of the droplet was recorded from its formation at the tip of the syringe to the point of contact with the substrate, release and equilibrium.

2.2. Characterization

The structural properties of all types of blocking layers were extensively characterized using secondary electron microscopy