Materials Science in Semiconductor Processing xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Patterning dye-sensitized solar cell photoanodes through a polymeric approach: A perspective

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ARTICLE INFO

Keywords:
Dye-sensitized solar cell
Patterning
Photolithography
Photoanode
Polymer electrolyte

ABSTRACT

Performances in terms of efficiency and stability of dye-sensitized solar cells (DSSCs) depend on several factors related to the preparation of the device components (electrodes and electrolyte). In particular, patterning techniques recently intruded in the third generation photovoltaic scenario with promising results. In this perspective, we introduce the most interesting strategies proposed for the patterning of photoanodes and cathodes. Afterwards, we propose a novel approach exclusively based on the use of polymeric materials. The resulting DSSC shows a power conversion efficiency equal to 5.33% measured under 1 sun irradiation, and retains the 96% of this value in a prolonged aging test (2000 h at 50 °C).

1. Introduction

In 1991, O'Regan and Grätzel proposed the dye-sensitized solar cell (DSSC) as the first solar conversion device based on (photo)electrochemical reactions and bearing a semiconductor/electrolyte interface as the core component [1–5]. In a global scenario dominated by silicon and emerging thin-film inorganic technologies, the scientific community welcomed the DSSC as a brilliant revolution in terms of novel approaches for solar energy harvesting [6–10]. An enormous research and development work has been carried out in these decades [11–16] and, at present, these hybrid organic-inorganic solar cells represent the best choice when low cost, architectural integration, and good performance particularly under low irradiance conditions and/or indoor environments are required [17–21].

The DSSC captures sunbeams to produce electrons, and it was conceived to mimic the photosynthetic process of chlorophyll [22,23]. To this purpose, a nanostructured semiconductor is typically deposited onto a conductive substrate and, subsequently, sensitized with a molecular dye able to absorb in the visible range. The semiconductor-dye system is called photonoade, and represents the core of the device [24–28]. The fabrication of photoanodes with strong light-harvesting ability, low exciton recombination, direct electron pathway and optimal interface with the electrolyte is still representing a key challenge for the DSSC community [29–33].

Patterning the geometry of micro-/nano-structures on DSSC electrodes represents a truly promising way to modify their optical, electrical and electrochemical properties. Furthermore, this approach could easily be scaled up by exploiting the class of patterning technologies developed in the last decades for manufacturing integrated circuits [34–37]. However, the know-how in this field is typically owned by research groups working in the electronic field (mainly for the development of sensors) [38–40], and has scarcely been shared with teams working in the DSSC sector. Indeed, Scopus database clearly shows that only 10 research articles have been published on patterning techniques applied to DSSCs over a total of 13,500 related publications, so far.

In this work, we demonstrate the usefulness of patterning to improve the photoanode/electrolyte interface in the presence of a quasi-solid polymer electrolyte. Indeed, quasi-solid electrolytes have been proposed as stable and non-volatile DSSC components to replace liquid solutions based on organic solvents, but their ability to properly wet the photoanode active material particles represents a major issue for solar cells performance. We show that by patterning a geometry of micropillars on the TiO_2 surface improves DSSC performance in terms of photocurrent and potential, due to the formation of a better photoanode/electrolyte electrochemical interface. Power conversion efficiency (PCE) equal to 5.33% has been obtained for a quasi-solid device, and was kept stable in a prolonged aging test (2000 h at 50 °C) maintaining the 96% of the initial value. Since patterning techniques are poorly detailed in the DSSC field so far, we also provide to the readers a brief initial overview of their recently demonstrated interesting aspects for solar cell fabrication.

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http://dx.doi.org/10.1016/j.mssp.2017.07.030
Received 1 February 2017; Received in revised form 25 June 2017; Accepted 31 July 2017

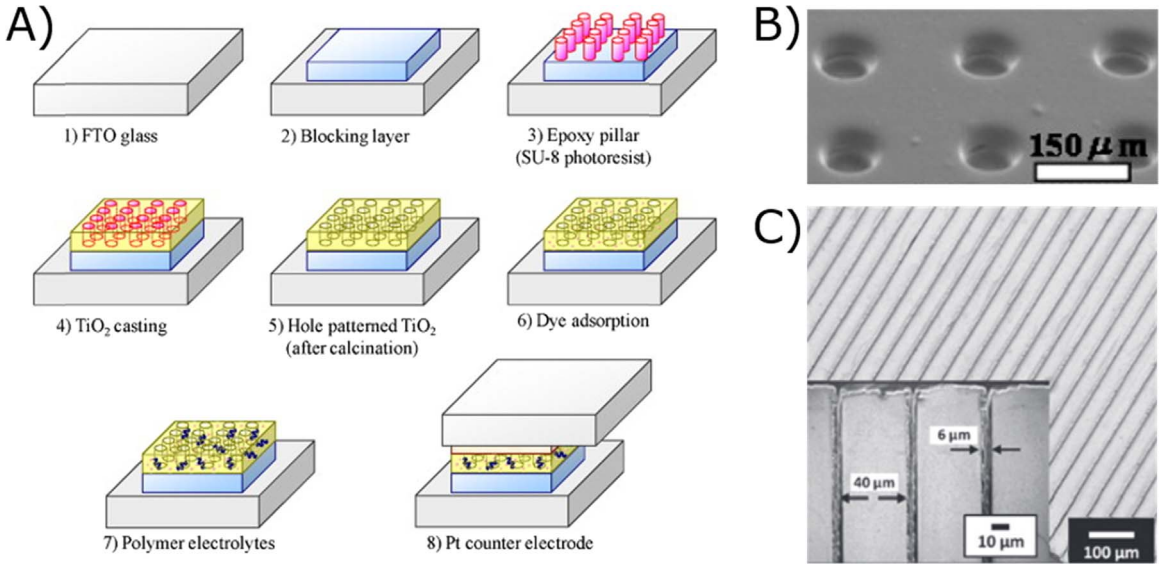

Fig. 1. A) Fabrication procedure of DSSCs with hole-patterned TiO_2 photoelectrodes and **B)** SEM image obtained after calcination. **C)** SEM images of as-fabricated 3D metal grid electrodes (inset shows dimension of the grid under 800× magnification). Adapted and reprinted from [34,36].

1.1. Patterning DSSC components: a brief overview

In 2010, Park *et al.* firstly proposed patterning techniques in the DSSC field [41]. They demonstrated a simple process to fabricate a hole-patterned TiO_2 electrode for a solid-state DSSC with the aim of enhancing cell performance by tailoring the characteristics of the electrode/electrolyte interface. At first, they pre-patterned the SU-8 photoresist onto a conductive glass, followed by the deposition of a nanocrystalline TiO_2 layer and calcination at 450 °C (Fig. 1**A**). Hole-patterned TiO_2 photoelectrodes (Fig. 1**B**) yielded enhanced solar energy conversion efficiency per dye loading compared to conventional non-patterned photoelectrodes. The performance improvement was attributed to increased transmittance through the electrode as well as better interfacial properties between the electrolyte and the electrode.

Patterning techniques can be applied not only to the TiO_2 layer, but also to the underlying fluorine-doped tin oxide (FTO) layer. To this purpose, Kong *et al.* carried out lithography and inductively coupled plasma etching to improve the PCE of DSSCs from 4.63% to 5.60% [42]. Scanning electron microscopy showed that, by using patterned FTO electrodes, an increased portion of TiO_2 particles could be involved in the electrochemical process; moreover, the contact between the TiO_2 layer and the conductive support was improved by patterning the FTO layer. The current-voltage curves and incident photon to current efficiency spectra showed that a significantly higher photocurrent was achieved in DSSCs with patterned FTO.

Chua *et al.* proposed the application of 3D metal grid electrodes as electron collectors useful to replace FTO-based electrodes. [43]. In their experiment, a very thin adhesion promotion layer was spin-coated onto a borosilicate glass substrate, followed by a 6 μm-thick photoresist (AZ9260). Lithography was done and titanium metal was deposited on top of this substrate by e-beam evaporation to form a 1 μm-thick film. Finally, a 10 μm-thick mesoporous nanoparticle TiO_2 paste was screen-printed directly on the 3D metal grid electrode. A PCE of 6.2% was achieved in the presence of a grid electrode (Fig. 1**C**) characterized by 6 μm width, 1 μm height and 40 μm spacing between grids.

The control sample made of the same materials, but fabricated onto a standard FTO glass, had a PCE of 7.1%.

In 2012, Yoo *et al.* demonstrated that patterning techniques can be useful also for designing efficient counter electrodes [44]. They compared a Pt-sputtered cathode deposited onto a patterned indium-doped tin oxide (ITO) glass with a conventional Pt counter electrode deposited by thermal reduction onto FTO glass. The patterned electrode (Fig. 2**A**) showed a lower charge-transfer resistance as compared to the reference cell, which led to a 7.6% improvement of its fill factor (*FF*). The long-term durability test performed for 1000 h at room temperature revealed that the patterned cell can retain up to 99% of its initial PCE, while the reference cell showed a 7.2% decay.

Since light harvesting efficiency plays an important role in improving the efficiency of DSSCs, many researchers typically employ a scattering layer on the photoanode [45–47]. As an alternative, Kim *et al.* proposed a different DSSC structure that employed a patterned reflection layer in the counter electrode to enhance the light harvesting efficiency by reusing reflected light [48]. Optical simulation analysis revealed that the light harvesting efficiency of a rectangular patterned reflection layer (Fig. 2**B**) was higher than that of other patterns, leading to a 22% enhancement in PCE when compared to reference cells.

López-López *et al.* used 1D gratings patterned on the surface of TiO_2 electrodes as a light harvesting strategy to improve the overall performance of DSSCs under both frontal and rear illumination conditions [49]. A soft-lithography-based micromoulding approach was employed to replicate a periodic surface relief pattern onto the surface of the electrode (Fig. 2**C**), which was later sensitized with a dye.

Large-scale patterned ZnO–ZnS core-shell nanowire arrays were designed and fabricated as photoanodes by Chen *et al.* [50]. By adopting a hexagonal symmetry (Fig. 3**A**), the resulting DSSCs demonstrated a maximum PCE of 2.09%, with an improvement of 140% as compared to the reference cells. It was attributed to the enhanced light-harvesting ability of the patterned photoanode, as well as to the remarkable double absorption caused by the introduction of an Al-based reflecting layer behind the counter electrode. Additionally, the ZnO core provided a direct electron pathway and the ZnS shell simultaneously reduced exciton recombination.

Wang *et al.* proposed a facile wet etching method to prepare patterned FTO electrodes [51], where the pattern depth was controlled by the etching time (Fig. 3**B**). The PCE gradually increased with increasing etching time, and a maximum of 7.71% was obtained after 240 s. Performance improvement was attributed to enhanced light harvesting and scattering due to larger amount of TiO_2 nanoparticles filled in the circular pattern, thus enhancing the amount of adsorbed dye.

A recent work in this field was published by Sajedi Alvar *et al.* [52], who utilized a micropatterned anode based on TiO_2 nanoparticles to achieve fast electron transport and low recombination rate in DSSCs.