Materials and Design 110 (2016) 18–26

Contents lists available at ScienceDirect

Materials and Design

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

TiO_2 anatase intermediary layer acting as template for ZnO pulsed electrodeposition

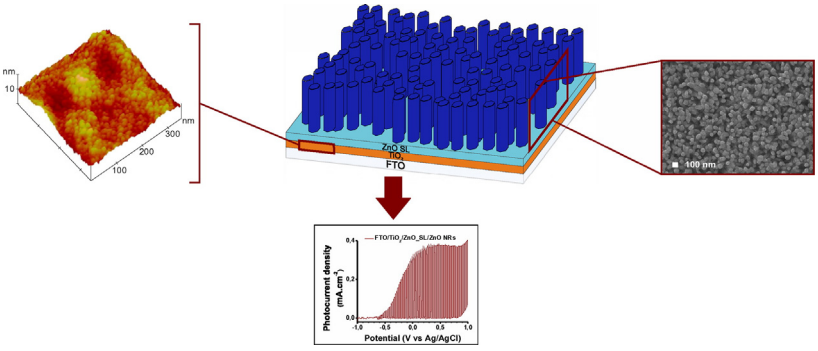
Tânia Frade [a], Killian Lobato [b], José F.C. Carreira [c], Joana Rodrigues [c], Teresa Monteiro [c], Anabela Gomes [a,*]

[a] Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[b] Instituto Dom Luiz, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[c] Departamento de Física e I3N, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

HIGHLIGHTS

- First report on the use of a TiO_2 intermediate layer for the growth n-type ZnO nanorod arrays by pulsed electrodeposition.
- Importantly, films are compared to those grown without a TiO_2 intermediate layer but with the same ZnO seed layer.
- In this case results show that nanorod density increases 3-fold to ~$165\mu m^{-2}$ and nanorod diameter decreases by 50% to ~40nm.
- Results also show that green intra-bandgap photoluminescence emission is suppressed indicating enhanced crystalline quality.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form 16 July 2016
Accepted 25 July 2016
Available online 26 July 2016

Keywords:
Nanostructures
Pulsed electrodeposition
ZnO
TiO_2 intermediate layer
Electron transfer
Photoelectrochemical behaviour

ABSTRACT

Zinc oxide nanorod (ZnO NR) films for photocatalytic and energy conversion applications were synthesized by pulsed electrodeposition. The films were prepared on modified fluorine-doped tin oxide (FTO) glass coated with thin layers of ZnO seeds and porous anatase titanium dioxide (TiO_2). The ZnO seed layers were prepared electrochemically, whilst the TiO_2 layers by spin-coating. Morphological and structural analysis of the films reveal the effect of the TiO_2 intermediate layers on ZnO NRs was to improve vertical alignment, increase spatial density and decrease diameter.

Room temperature photoluminescence (PL) results show that the ZnO NRs exhibit near band edge recombination and deep level emission in the green and red spectral regions. The green emission was almost suppressed for ZnO NRs grown using the TiO_2 intermediate layer followed by two step electrodeposition of ZnO.

The prepared films demonstrated photoelectrochemical behaviour in aqueous electrolytes. Additionally, the ZnO NRs prepared with a TiO_2 intermediate layer demonstrated increased stability to photo-dissolution.

1. Introduction

Zinc oxide (ZnO) is a direct bandgap n-type semiconductor which is transparent in the visible range of the electromagnetic radiation spectrum. Due to its electrical and optical characteristics (e.g. high binding

* Corresponding author.
E-mail address: abmg@fc.ul.pt (A. Gomes).

http://dx.doi.org/10.1016/j.matdes.2016.07.122
0264-1275/

energy of 60 meV at room temperature for the free exciton), it is one of the most promising materials for optical and electronic applications [1,2]. For photovoltaic (PV) applications ZnO has been successfully used in dye-sensitized solar cells [3,4], and recently in perovskite solar cells [5–7].

Different ZnO morphologies, such as nanowires, nanorods, nanosheets, nanobelts and nanotubes can be obtained depending on the growth conditions. Of these morphologies 1D ZnO nanostructures should be the most favourable as electron collecting layers because they combine direct electron transport pathways with large surface areas [8,9]. The 1D ZnO nanostructures can be prepared by a variety of processes, e.g. sputtering [10], chemical vapour deposition (CVD) [11], atomic layer deposition (ALD) [12], metal organic chemical vapour deposition (MOCVD) [13], sol-gel synthesis [14,15], spray pyrolysis [16], and electrodeposition [17,18]. Due to the a) low temperatures involved (<100 °C), b) growth orientation control of ZnO thin films and c) scalability and hence economic viability, electrodeposition has attracted significant attention for the formation of 1D ZnO nanostructures [19,20]. There are several reports about the orientation control of ZnO thin films prepared by electrodeposition [8,21]. Previous studies using electrodeposition technique employed a constant potential/current, and ZnO films with hexagonal single-crystal columns were attained, which is the most typical morphology obtained by electrodeposition [22–24]. However, the application of a constant potential/current has limitations when tuning some features of ZnO films. Pulsed electrodeposition, for example, has the advantage of promoting nucleation, enabling the formation of fine crystals. This is achieved by the opportunity of adjusting pulse parameters independently over a wide range. The result is the additional diffusion of reacting species, which plays an important role during electrodeposition [19,25,26]. Consequently, by controlling pulse parameters, it should be possible to further optimise films to the desired morphologies. For the electrolyte composition, most reports in the literature use dissolved oxygen as the oxidant [27], although electrodeposition of ZnO from nitrate-based electrolytes has also been extensively studied [22,28]. When compared to the use of O_2 [20,29] or H_2O_2 [30], the use of nitrate-based electrolytes has the advantage of reducing the need for convection and the addition of an extra oxidant.

The substrate onto which the electrodeposition occurs is also a fundamental parameter that defines film growth morphology. For PV application the substrate tends to be a transparent conducting oxide (e.g. FTO or ITO). However, this can be modified with intermediate (or buffer) layers to model ZnO film growth [31–34].

Using a TiO_2 thin layer as a template, ZnO electrodeposition in one or two steps, i.e., with or without a ZnO seed-layer, seems to allow for better control of the nucleation step, which is a crucial factor for ZnO vertical growth [35]. To the best of our knowledge, the use of TiO_2 as an intermediate layer for pulsed electrodeposition of ZnO nanorods has never been reported. As such, the influence on morphology, structure, optical and electrical characteristics of this type of intermediate layer was studied for the pulsed electrodeposition of ZnO nanorods.

2. Experimental procedures

2.1. Pulsed electrodeposition of ZnO 1D nanostructures onto different substrates

The substrates onto which the ZnO nanorods were grown were of four types: 1) bare fluorine-doped tin oxide coated glass (Pilkington TEC 15, 12–14 Ω/□); 2) FTO coated with a ZnO seed-layer; 3) FTO coated with a TiO_2 film and 4) a TiO_2 film coated with a seed-layer of ZnO. These modified substrates are hereafter designated as FTO/ZnO_SL, FTO/TiO_2 and FTO/TiO_2/ZnO_SL respectively.

The FTO substrates were cleaned by ultra-sonicating (Elma S30) sequentially for 15 min in liquid neutral soap, acetone and ethanol (95%). In between sonications the electrodes were rinsed in abundant deionised water (18.2 MΩ.cm). The substrates were then dried in nitrogen (N_2) flux.

The TiO_2 layers (c.a. 100 nm in thickness) were prepared by spin-coating (500 rpm for 3 s and 2000 rpm for 30 s) using a solution of 0.15 M titanium diisopropoxide bis(acetylacetonate) (75%, Aldrich) in 1-butanol (Aldrich). Upon deposition the samples were then moved into an oven and heated in air at 125 °C for 5 min. Upon cooling to room temperature (RT), the same spin-coating and heating process was repeated twice, however with a more concentrated solution of 0.30 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol. Finally and upon rinsing in deionised water, these were annealed in air at 500 °C for 15 min inside a muffle furnace. The heating rate was 5 °C.min^{-1} whilst cooling to RT occurred naturally within the furnace.

The ZnO seed-layers (<100 nm thickness) were prepared electrochemically by applying −1.3 V vs Ag/AgCl for 30 s on FTO and FTO/TiO_2 modified substrate surfaces, using an aqueous solution of 10 mM $Zn(NO_3)_2 \cdot 6H_2O$ (98.0%, Sigma-Aldrich) and 5 mM KCl (Sigma-Aldrich) prepared with deionised water as electrodeposition bath, solution pH 6.4. The temperature of the solution was maintained at 70 °C. A Gamry R600 potentiostat/galvanostat was used to perform the electrodeposition processes.

Pulsed electrodeposition of ZnO 1D nanostructures was carried out in a single compartment glass cell using as the working electrodes FTO, FTO/ZnO_SL, FTO/TiO_2, and FTO/TiO_2/ZnO_SL. The electrode area in contact with the electrolyte was a square measuring 2.25 cm^2. A graphite foil (9 cm^2 area) was used as counter electrode and Ag/AgCl (saturated KCl) electrode as reference. The working and counter electrodes were placed parallel to each other separated by a distance of 2 cm. The electrolytic baths were the same as used for ZnO seed-layer electrodeposition. ZnO electrodeposits were prepared by applying a potentiostatic square wave for 60 min. Each cycle consisted of 0.25 s at −1.0 V vs Ag/AgCl and 1 s at 0.0 V.

Finally and upon rinsing in deionised water, the as deposited films were annealed in air at 450 °C for 1 h inside a muffle furnace. As before, the heating rate was 5 °C.min^{-1} whilst cooling to RT occurred naturally within the furnace.

Resultant film thickness varied between c.a. 500 nm and 800 nm depending on the substrate used.

2.2. Characterization

2.2.1. Voltammetric studies

Cyclic voltammetry was undertaken to understand the effect the four differing substrates have on ZnO film growth.

The electrolyte composition and conditions and electrode setup were identical to those used for pulsed electrodeposition. Voltammograms were acquired by scanning three times between the open-circuit potential (~0.2 V) and −1.3 V vs Ag/AgCl. The scan rate was 10 mV.s^{-1}.

2.2.2. Morphological, structural and optical characterization

The morphology of ZnO 1D nanostructures was investigated by field-emission scanning electron microscopy (FEG-SEM JEOL JSM-7001F).

The surface morphology of the TiO_2 films was imaged by atomic force microscopy (Nanoscope IIIa). Acquisition was in tapping mode at a scan rate of 1.5–1.8 Hz. The tips were etched silicon with a resonance frequency of ~300 kHz (TESP, Bruker).

The structural characterization of the films was carried out by X-ray diffraction (XRD), on a Philips PANalytical PW 3050/60 X'Pert PRO (θ/2θ) equipped with an X'Celerator detector and X'Pert Data Collector (v2.0b) software, using a monochomatic Cu-K_α radiation as the incident beam, operating at 40 kV and 30 mA. XRD patterns were obtained by continuous scanning in the 2θ-range from 20 to 90°. The preferred orientation of the ZnO 1D nanostructures was estimated from the X-ray data according to the methodology developed by Bérubé et al. [36], considering the three Miller indexes of the four usually used to describe the