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Deposition of porous titanium oxide thin films as anode material for dye sensitized solar cells

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ABSTRACT

Crystallized nanoporous TiO_2 thin films were synthesized by combining reactive magnetron sputtering and Glancing Angle Deposition (GLAD). The growth temperature, the bias voltage and the rotation speed of the substrate were studied with the aim to grow nanoporous films presenting anatase constitution which are suitable for Dye Sensitive Solar Cells (DSSC) applications.

By fixing the tilt angle at 85°, we have shown that an increase of the growth temperature up to 450 °C leads to the formation of nanoporous anatase film with a grain size up to 24 nm while by applying a bias voltage leads to a densification of the films as evidenced by scanning electron microscopy and by X-ray diffraction. On the other hand, by rotating the substrate (from 0.1 to 10°/s) during the deposition process, films with larger columns and higher surface roughness (from 45 to 60 nm) were obtained due to an enhanced shadowing effect.

Preliminary dye impregnation experiments have shown that the highest light absorption values are obtained for the films prepared without bias and with no rotation, which is supported by the microstructure of these films presenting the highest porosity. These films, presenting an anatase constitution, are potentially good candidates as an anode in DSSC applications.

1. Introduction

Nowadays, the efficient use of renewable energies represents a major economic and environmental issue. This is obviously also true for the solar energy, by far the most important of them in term of quantity. In this context, among the many advantages of the dye-sensitive solar cells (DSSC), their cheap production cost and good performance at low illumination and high temperatures are very interesting [1–5]. The highest efficiencies [2] are around 10% and, more recently, the fabrication of solid state DSSCs with 15.0% efficiency was announced by Graetzel [6]. Much of the shortfall is due to the poor absorption of low-energy photons by available dyes. Considerable efforts have been made to develop dyes and dye mixtures that absorb better at long wavelengths but, so far, with little success [7]. Another option for improving the absorption of red- and near-infrared light is by thickening the nanoparticle-based film to increase its optical density. This approach is unsuccessful because the film thickness begins to exceed the electron diffusion length through the nanoparticle network [8]. Indeed, the photo-anode of a DSSC is often composed of an array of TiO_2 nanoparticles. In the latter situation, the charge transport is limited by trapping–detrapping processes in which both morphological disorder and energy play a role [9]. The structural disorder at the nanoparticle boundaries enhances the scattering of free electrons and thus reduces the electron mobility [10]. So, even if these nanoporous TiO_2 films have large surface areas (around 56 m^2/g for P25 [11]) and allow an efficient collection of photons, the electron transport is a limiting factor for the conversion efficiency. Ideally, the porous film must have interconnected particles, to allow the percolation of the injected electrons [12].

A potential alternative would be a porous crystalline TiO_2 thin film with nanoscale ordered photo-anode architectures, such as nanotubes [12–14], nanorods [15–17] and nanowires [8,18]. The

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main potential advantage of these structures relies on a better collection of charges as they provide a more direct path towards the external circuit so that recombination at the boundary grains and exposure to the electron acceptors in the electrolyte is avoided. In this way, faster transport and a slower recombination rate lead to a minimization of charge losses. However, the synthesis of these porous materials by sol-gel method [8,19], anodic oxidation [20], or, electron beam evaporation [21], usually leads to amorphous structures which require additional annealing treatments to crystallize TiO_2 films.

The crystalline constitution of TiO_2 is also important in order to optimize the charge separation and transport in a DSSC. The anatase phase of TiO_2 is usually preferred as the electron acceptor in DSSCs, partly due to the difference in the band-gap value of anatase and rutile TiO_2 polymorphs. The anatase conduction band is 0.2 V more negative than that of rutile, a larger maximum photovoltage can be thus obtained for anatase (assuming that the same redox mediator is employed) [22,23]. Nevertheless, it has been shown that a mixture of rutile and anatase TiO_2 crystals could enhance the photo-current and the overall solar conversion efficiency [24]. In this work, the best photo-current and overall solar conversion efficiency were obtained for a rutile content in the film around of 13% by weight. This was explained by a synergistic effect between anatase and rutile crystal. Interfacial electron transfer occurs from rutile to anatase: photo-excited electrons injected into rutile can be transferred to the conduction-band of anatase [24]. With anatase and rutile in close contact, photo-excited electrons and holes are preferentially trapped in the anatase and the rutile phases inhibiting the detrimental electron–hole recombination [25]. However, the increase of the rutile concentration above this percentage appears to be detrimental to the DSSCs because the diffusion coefficient of conduction-band electrons in rutile is significantly smaller than that in anatase [26].

In order to generate such a porous coating while controlling the phase constitution, we combined Reactive Magnetron Sputtering (RMS) and Glancing Angle Deposition (GLAD). The magnetron sputtering process allows precise control of the microstructure and related properties of the film such as its density, adhesion, surface roughness and crystallinity and it is also cost effective for industrial applications, overcoming the current barriers in other film deposition processes [27]. Anatase TiO_2 thin films have already been grown successfully at room temperature on glass substrates using dc magnetron sputtering in reactive mode [28]. The crystallization of TiO_2 films at room temperature is mainly promoted by energetic particle bombardment (electrons, atoms, ions, molecules and even charged clusters) during sputtering. It has been demonstrated that deposition parameters have great impact on the properties of these films. Indeed, a sputtered thin film which is crystallized by a supply of energy will be dense and therefore the use of GLAD is necessary in this case. Ballistic shadowing is the foundation of GLAD-based thin film engineering. Such shadowing is only possible if the incoming vapour flux is well collimated. In this method, the substrate can be tilted with an angle (α) and/or rotated with an angle (φ) step by step or with a continuous angular speed (φ_s) in order to generate a columnar porous thin film (Fig. 1). The GLAD process enables the growth of columnar thin films with specially engineered nanostructures. These films are extremely porous and consist of isolated columns that can take the form of, for example, helices, vertical posts and polygonal spirals [29]. The porosity (inter-columnar space) and the columnar tilt angle (β) can be tuned to have open pores (mesopores) to increase the specific surface area and improve the dye and electrolyte penetration in the case of specific DSSC applications [30,31].

The combination of MS and GLAD techniques have already been used to synthesize nanostructured thin films comprising different types of materials such as chromium [32,33], titanium [34–36], and titanium dioxide [37,38]). Z. Michalčík et al. [37] prepared TiO_2 thin films by the MS and GLAD methods in order to increase the photocatalytic activity. Their nanostructured films were characterized by a higher surface roughness and a substantially higher relative specific surface compared with films prepared by conventional MS. For the application of the anatase films as photo-anodes in dye-sensitized solar cells, Su-Il In et al. [38] prepared vertically aligned anatase TiO_2 nanowire arrays on FTO (Fluorine doped Tin Oxide) coated glass substrates via pulsed DC MS at low temperature. They found a preliminary photo-conversion efficiency of 1.07% for their nanowire-based photo-anode 3.6 μm thick. This is slightly more efficient than single crystals or flat electrodes of polycrystalline films of tin-oxide or titanium-oxide used like a photo anode. In spite of the efficient electron injection into the semiconductor, the light harvesting efficiency was very small and the efficiencies of the solar cells were extremely low (below 1%) [39,40]. Nanostructures, such as vertically aligned nanowires, provide direct pathways for electron transport and, when used as photo electrodes, improve the electron diffusion-length, electron life-time and diffusion-coefficient. However, they have a fundamental disadvantage: they do not provide the necessary specific surface area for dye adsorption, resulting in DSSCs with poor efficiencies. Therefore, in this work, the interrelated and nonlinear parameters of both MS and GLAD were varied in order to determine an experimental window allowing the growth of porous TiO_2 films presenting an anatase and/or rutile crystalline structure that allow significant grafting of dye molecules, which were a conjugated polymer, namely regioregular poly(3-hexylthiophene, P3HT), in this work.

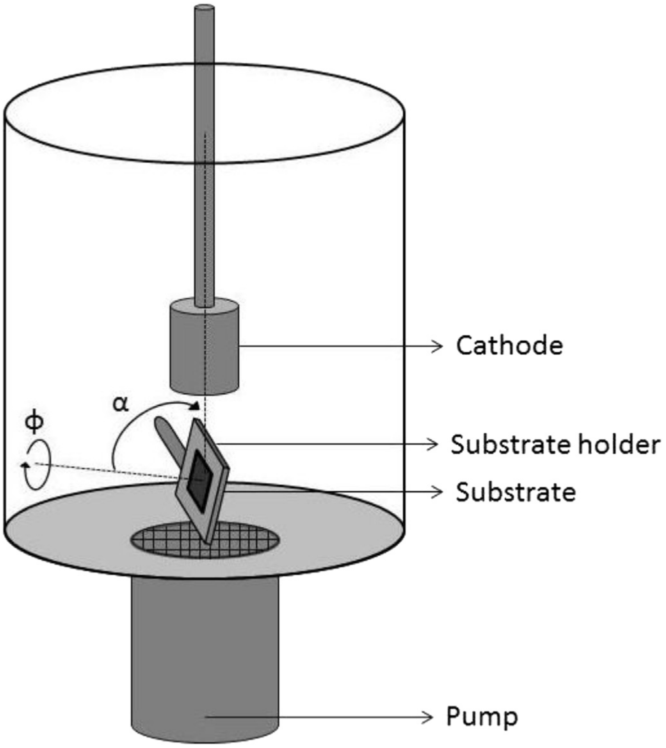

Fig. 1. Experimental setup diagram of the deposition chamber.

Conjugated polymers are a special class of material gathering the advantages of plastics and semiconductor properties [41]. The conjugated double-bonds in the main chain can interact with light and determine the optoelectronic properties of the polymers [42,43]. Among conjugated polymers, P3HT is of major interest