Thin Solid Films 592 (2015) 276–280

Contents lists available at ScienceDirect

Thin Solid Films

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

Control of ordered mesoporous titanium dioxide nanostructures formed using plasma enhanced glancing angle deposition

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ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 20 April 2015
Accepted 21 April 2015
Available online 28 April 2015

Keywords:
Glancing angle deposition
Plasma ion assist deposition
Ordered mesoporous nanostructures
Control of mesoporous morphology

ABSTRACT

Three dimensional nanostructures of mesoporous (pore diameter between 2-50 nm) nanocrystalline titania (TiO_2) were produced using glancing angle deposition combined with plasma ion assisted deposition, providing plasma enhanced glancing angle deposition eliminating the need for post-annealing to achieve film crystallinity. Electron beam evaporation was chosen to deposit nanostructures at various azimuthal angles, achieving designed variation in three dimensional nanostructure. A thermionic broad beam hollow cathode plasma source was used to enhance electron beam deposition, with ability to vary in real time ion fluxes and energies providing a means to modify and control TiO_2 nanostructure real time with controlled density and porosity along and lateral to film growth direction. Plasma ion assisted deposition was carried out at room temperature using a hollow cathode plasma source, ensuring low heat loading to the substrate during deposition. Plasma enhanced glancing angle TiO_2 structures were deposited onto borosilicate microscope slides and used to characterise the effects of glancing angle and plasma ion energy distribution function on the optical and nanostructural properties. Variation in TiO_2 refractive index from 1.40 to 2.45 (@ 550 nm) using PEGLAD is demonstrated. Results and analysis of the influence of plasma enhanced glancing angle deposition on evaporant path and resultant glancing angle deviation from standard GLAD are described. Control of mesoporous morphology is described, providing a means of optimising light trapping features and film porosity, relevant to applications such as fabrication of dye sensitised solar cells.

1. Introduction

Titania (TiO_2) and its compounds have been extensively studied owing to their wide applications in particular as photocatalysts, based on their strong oxidizing abilities for decomposition of organic pollutants [1,2]. TiO_2 has three forms, (i) Anatase where the crystal structure is tetragonal with dipyramidal habit, (ii) Rutile also tetragonal but with prismatic habit and (iii) Brooktite which has an othorholmbic crystalline structure. Rutile is principally used as a pigment and Anatase is the preferred form as a relatively cheap photocatalyst with a high surface area, no toxicity and photochemical stability [3–7].

Highly structured mesoporous nanocrystalline materials are currently being researched principally for dye sensitised solar cells (DSSC) [8, 9]. However, the current self assembly manufacturing methods used for DSSC's are limited in achieving thicknesses less than 1 μm in a single step and less than 4 μm in multiple steps, without introducing unacceptable opacity. Other limitations of the self assembly process are lack of intrinsic light trapping properties and relatively poor electron transport routes for effective photovoltaic performance [8, 9].

Although thicker films have been produced they do not have a long range mesoporous structure, limiting fast electron/photon transportation characteristics of mesoporous oxides and thus limiting their application to DSSCs and other photocatalytic applications [10].

Various other methods or techniques have been investigated for low temperature growth of high quality crystallized TiO_2 with varying degrees of success [1–3]. However, the films prepared using these methods are often amorphous requiring post annealing to improve the crystallinity of the as-deposited film. A major drawback is annealing temperatures, generally > 400 °C, precluding use of temperature sensitive substrates and the requirement for a separate high temperature processing stage. There are also significant increases in grain size and changes in surface chemistry, affecting the optical and photocatalytic properties of the films [11].

Desirable morphology would involve synthesising nanostructures with a higher degree of order than nanoparticles and have mesoporous channels and nanocolumns aligned parallel to each other and vertically inclined to maximise light trapping and electron transport. This would

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http://dx.doi.org/10.1016/j.tsf.2015.04.063
0040-6090/

facilitate light trapping and allow easier access to film boundaries allowing in the case of photovoltaic cell fabrication the p-n junction to form with better control.

Highly ordered mesoporous structured anatase TiO_2 may be obtained without the need of high temperature processing using plasma ion assisted deposition (PIAD) [1] combined with glancing angle deposition (GLAD) [12] providing plasma enhanced glancing angle deposition (PEGLAD). The PIAD process is not applied directly to TiO_2 mesoporous growth as it is generally considered that the resultant increased density and reduction in measured surface roughness are contrary to the requirements of a mesoporous structure.

In this paper mesoporous structured anatase TiO_2 samples were prepared at room temperature using the PEGLAD process, with granular Ti_3O_5 as source material. PEGLAD film optical and structural performance as a function of ion energy distribution function, ion current density and GLAD angle are described. The resulting desirable morphology would have mesoporous channels and, or nano-columns aligned parallel to each other and in line with the photon and electron current. Such structures provide easier access to film and grain boundaries, allowing for example p-n junction formation under better control and reduce interfacial charge re-combination [13, 14].

2. Experimental Procedure

25 mm x 75 mm x 1 mm thick glass substrates were cleaned using an ultrasonic machine (Optimal UCS40). A TiO2 layer was deposited on the substrate using PIAD [15] combined with Glancing Angle Deposition (GLAD) [16] (deposition system SATIS MS LAB 380). Fig. 1a shows the base plate layout within the Satis MS Lab 380 coater and Fig. 1b shows the geometry of the plasma source and electron beam interaction. Fig. 1c shows typical GLAD hardware [16] enabling change in plasma ion and evaporant flux angle with respect to the substrate.

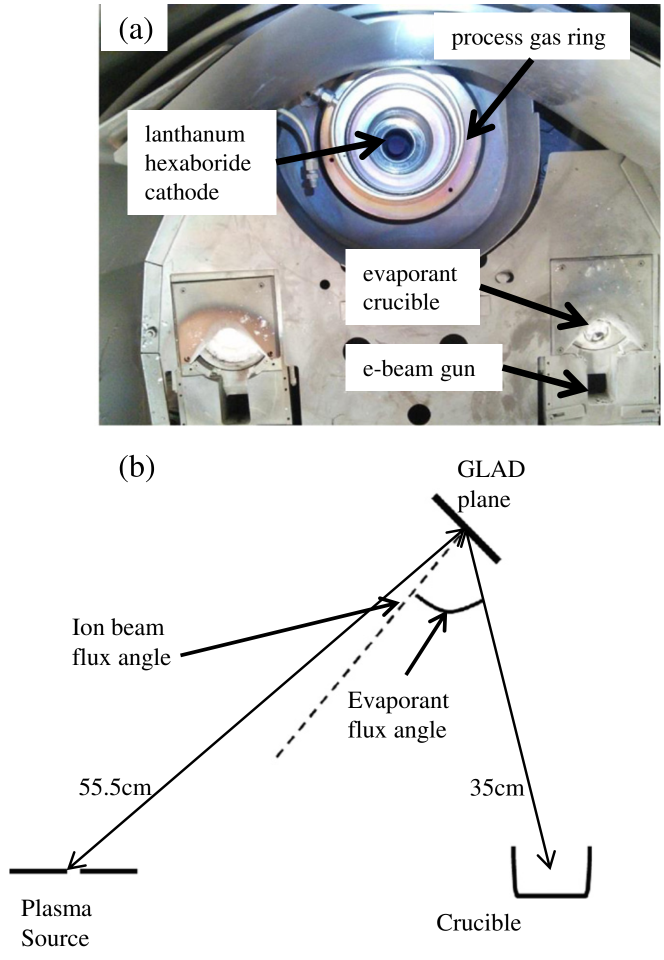

Fig. 1. (a) Satis Box coater baseplate configuration fitted with ebeam evaporation and a hollow cathode plasma source and (b) plasma source/e-beam gun/substrate geometry (c) GLAD hardware indicating capability to change substrate angle with respect to source.

The plasma source is based on a thermionic hollow cathode LaB6 [15] with O_2 and Ar gas flow rates set at typically 10 sccm each during evaporation, resulting in a deposition pressure of 20×10^{-3} Pa with a base chamber pressure of 50×10^{-6} Pa. Ti_3O_5 granules (Materion Inc., 99.9 %) were electron beam evaporated and deposited onto glass substrates at room temperature.

Ion beam energy was set at 5 eV, 20 eV, and 50 eV, ion current density adjusted between 0.63 mA/cm^2 and 0.93 mA/cm^2 and apparent evaporant flux glancing angles from 0 to 110 degrees were used at a constant deposition flux.

3. Characterisation

The crystalline structure of the TiO_2 layers was determined by X-ray diffractometry (XRD) (Siemens D5000) with CuK α radiation (40 kV, 30 mA). The diffraction angle was set between 20 degrees and 60 degrees with 1 scan (count) per second at 0.2 increments. The morphology of the surface and cross-sections were determined by scanning electron microscope (SEM) (Hitachi S-4100) with micrographs taken at 20 kV.

A comparison was made between films deposited at a constant evaporant flux angle with and without PIAD.

A comparison of resulting cross sectional columnar growth morphology (Hitachi 4100S electron microscope) was also made between films deposited at various azimuthal angles, IEDF and ion current densities.

The refractive index was determine by measuring transmittance and reflectance as a function of incident angle (Aquila nkd 8000 variable angle spectrophotometer) using best fit to a Drude–Lorentz model [17]

4. Results and Discussion

4.1. Crystallinity - X-Ray Diffraction

Fig. 2(a) shows XRD results for a sample deposited at room temperature but enhanced with plasma ion beam set variously at 0.63 mAcm^{-2}, 0.78 mAcm^{-2} and 0.93 mAcm^{-2} [18]. In each case, anatase TiO_2 peaks of 101 were observed increasing in magnitude with increasing ion energy. Fig. 2(b) shows XRD results for an amorphous sample of TiO_2 deposited by GLAD without PIAD at room temperature.

4.2. Cross Sectional Morphology - Electron Beam Microscopy

Fig. 3 shows SEM images of the surface and cross-section of the samples. It can be seen from Fig. 3 there are differences between GLAD (left) and PEGLAD (right)). With PEGLAD the nano columns of TiO_2 are thicker but shorter producing a thinner TiO_2 layer.

Fig. 4a and b show column width and height respectively for PEGLAD TiO_2, as a function of ion current density for two ion energies. Results indicate TiO_2 nano column length decreases with increase in ion beam energy and current density and conversely width of TiO_2 nano-columns increases with increasing ion beam energy and current density, providing a ready means to control column height, width and orientation.

4.3. Refractive Index

As increasing refractive index is linked to decreasing porosity we can infer from Fig. 5 that porosity is decreasing with increasing plasma ion energy. This corresponds with the SEM images in fig. 3 showing that at constant deposition rates addition of plasma energy results in increased column width with a thinner layer and hence higher packing