Thin Solid Films 568 (2014) 81–86

Contents lists available at ScienceDirect

Thin Solid Films

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

An oblique angle radio frequency sputtering method to fabricate nanoporous hydrophobic TiO_2 film

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ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 31 July 2014
Accepted 8 August 2014
Available online 14 August 2014

Keywords:
Oblique angle sputter deposition
Titanium dioxide
Thin films
Columnar array
Hydrophobic surface

ABSTRACT

In this work, we investigate growth of ordered arrays of amorphous TiO_2 nano-columns by using radio frequency sputter deposition technique. The as-prepared thin films were characterized by atomic force microscopy, field emission scanning electron microscopy, X-ray diffraction, and ultraviolet–visible spectroscopy. The nano-columnar films are found to be porous in nature which results from glancing angle sputter deposition. In fact, porosity has a linear relationship with increasing deposition angle. Reflectance of the thin films is also studied as a function of porosity. In addition, contact angle measurements demonstrate the roughness dependent transition from a hydrophilic to a hydrophobic TiO_2 surface.

1. Introduction

Recently ordered arrays of nanostructures have started drawing attention due to their fascinating applications in photonic crystals [1,2], surface-enhanced Raman spectroscopy [3], biosensors [4], and so on. Either of additive or emergent property of a nanostructure array shows some advantageous properties compared to a single nanostructure and thus makes it more useful for device application [5]. One of the major reasons behind the attractive usages of nanostructure arrays is the large effective surface-to-volume ratio, which enhances all the surface related properties and allows more surface atoms to participate in the surface reactions. Porosity of nanostructured thin films is an important parameter which controls several physical properties such as refractive index [6], catalytic properties [7] etc.

Different growth techniques including surfactant assisted growth can generate various morphologies with controlled porosity [8]. Along with the most promising synthesis technique like lithography [9–11], the use of oblique angle deposition to control film morphology as well as film porosity is the well accepted trend in research to grow ordered, self-assembled nanoporous thin films [12]. Oblique angle deposition technique basically works on the shadowing effect [13]. According to Tang et al. [14], the shadowing effect originates from a non-normal incident flux where the obliquely incident particles cannot reach the lower lying surface points because they are "self-shadowed" by taller surface features in the neighbors. Electron beam evaporation technique is widely used to fabricate nanostructured materials with oblique deposition and controlled substrate motion to tailor structures, such as slanted columns, nanorods, zigzags, spirals, or screws on the nanometer scale [15,16]. Very recently, glancing angle sputter deposition is given preference among other techniques because this technique is suitable for large area deposition with high uniformity and reproducibility along with good adhesivity to the substrate.

In this work, we have chosen TiO_2 since it has wide applications related to photocatalysis [17], sensors [18], photovoltaic cells [19], and self-cleaning and antifogging properties [20,21]. The columnar microstructures of glancing angle deposited metal-oxide films leads to a remarkable amplification in the surface area when compared to a dense flat film. The enhanced surface area of such films has been exploited in a variety of applications. Kiema et al. [22] designed a dye sensitized solar cell (DSSC) using TiO_2 nanostructures with a conversion efficiency of 4.1%. Steele et al. [23] developed high speed humidity sensors using columnar metal-oxide films.

In this paper, we have focused on the growth of amorphous nano-columnar array of TiO_2 thin films on silicon substrates. Amorphous TiO_2 is considered to be a potential candidate for use as an anode material of high-rate dischargeable and chargeable lithium ion batteries [24,25]. Kang and his co-workers [26] synthesized nano-columnar TiO_2 thin films by radio frequency sputter deposition and studied photo- and electro-chemical characteristics where they attempted to compare density and porosity of the nanocolumnar TiO_2 thin films at different

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http://dx.doi.org/10.1016/j.tsf.2014.08.005

temperatures. Here, we have studied the correlation of porosity and reflectance of the amorphous nano-columnar TiO_2 thin films as a function of deposition angle. We find that with increasing oblique angle of deposition, porosity of the nano-columnar TiO_2 films increases and finally saturates whereas refractive index of the films show an opposite trend. Using atomic force microscopy (AFM) we have also investigated the growth dynamics of the nano-columnar arrays as it has significant contribution for porosity generation. In addition, we have also explored the columnar morphology driven transition from hydrophilic to hydrophobic nature of the sputter deposited TiO_2 thin film surfaces. The hydrophobic surface is one of the basic routes of self-cleaning where water droplets slide and roll over the surface and in turn clean the surface. Hydrophobic surfaces can be achieved through control of either chemical composition or structural modification of the surfaces [27]. Therefore, we aim to understand the growth dynamics of nano-columnar arrays of TiO_2 thin films which is quite important since surface roughness is dependent on growth and it is known to play an important role to control many of physical, chemical, and biological processes which occur at surfaces. We have grown TiO_2 films with well-defined roughness and characterized them to finally correlate it with their optical and surface properties with roughness. It may be mentioned that such nanoporous TiO_2 thin films having tunable refractive index (with reasonably good anti-reflection property) and hydrophobic nature (with good self-cleaning property) will enhance the efficiency and stability of solar cells, respectively [28–30]. This growth strategy may also be extended to the fabrication of similar structures using different materials.

In fact, we will show that the porosity of the TiO_2 nanorod films can be controlled by changing the angle of deposition which in turn not only change the refractive index of the film from 2 to 1.54 but also change the hydrophobic nature. This study is very important, in particular for solar cell applications, because low refractive index gives an excellent anti-reflection and on the other hand hydrophobic nature will enhance the stability of the solar cell.

2. Experimental detail

Thin films of TiO_2 were deposited in radio-frequency magnetron sputtering setup (Excel Instruments, India) at normal and different oblique angles of incidence on *p*-type Si (100) substrates (B-doped, resistivity of 0.01–0.02 Ω cm). Before deposition, the substrates were ultrasonically cleaned in acetone, propanol, and de-ionized water to remove organic contaminants and were air dried. Commercially available TiO_2 disk (99.9%) of diameter 50 mm (Testbourne, UK) was used as the target material. The deposition chamber was evacuated to a base pressure of 5×10^{-5} Pa. Sputtering was performed in pure Ar atmosphere at a pressure of 5×10^{-1} Pa and by using radio frequency power of 50 W (Cesar, Advanced Energy, USA). The target-to-substrate distance was kept fixed at 80 mm for every deposition. The deposition time was chosen in a way so that it yields film thickness between 80 and 100 nm, following thickness calibration with a surface profilometer (XP-200, Ambios, USA). Depositions were carried out at room temperature (RT) and at three angles, viz. 0°, 45° and 87° (between the substrate surface and the mean direction of the sputtered flux). During each deposition substrates were continuously rotated at a constant speed of 3 rpm for all the films.

The crystalline nature of the films was investigated using a PANalytical X'Pert Pro powder X-ray diffractometer (XRD) with Cu-Kα radiation. Detailed studies on microstructure of the films were performed using a field emission scanning electron microscope (FESEM) operated at 20 kV (Zeiss Ultra FESEM, Germany). Film morphologies were studied by ex-situ atomic force microscopy (AFM) in AC™ mode (MFP3D, Asylum Research, USA). Silicon probes, having ~10 nm tip diameter were used for imaging. For each sample, a large number of AFM micrographs (having pixel size of 512 × 512) were collected from different regions to check the uniformity of the surface morphology. Root mean square (rms) surface roughness (w) and all the growth exponents were extracted using the WSxM software application, version 5.0 Develop 3.1, Nanotec Electronica S.L. Film thicknesses were measured by a surface profilometer with measurement accuracy of ±10 nm. Reflectance spectra of TiO_2 thin films were recorded using an ultra violet–visible–near infrared (UV–vis–NIR) spectrophotometer (3101PC, Shimadzu, Japan). Water contact angles were measured (OCA15EC, Dataphysics, Germany) at RT from at least three different locations to check the consistency.

3. Results and discussion

Fig. 1 presents the XRD data of as-prepared TiO_2 films deposited at all three deposition angles of 0°, 45° and 87°. The diffractograms do not show any peak, which indicates that as-prepared films are amorphous in nature in all three cases.

Fig. 2 shows scanning electron microscopy images (SEM) which depict the change in surface morphology of the as-prepared films with variation in the deposition angle. Fig. 2(a) and (b) are plan-view SEM micrographs corresponding to films deposited at 0° and 87°, respectively. In the case of normal incidence [Fig. 2(a)], a granular microstructure is observed and the film is largely uniform. In contrary, the film deposited at 87° shows the presence of porosity spread over the entire surface [Fig. 2(b)]. The cross-sectional view [Fig. 2(c)] of the same film (i.e. the one deposited at 87°) shows the presence of well-aligned nano-columns of height 80–90 nm and width 15–20 nm. It is also seen that the tips of the nano-columns are wider than their bases. This kind of widening of the top end compared to the base occurs due to the fast rotation of substrate applied during sputter deposition in glancing angle mode [16,31]. In case of normal incidence (i.e. for 0°) no such nano-columnar structure is observed in the cross-sectional view (micrograph not shown).

Fig. 3 shows AFM images of TiO_2 thin films deposited at incidence angles of 0°, 45°, and 87°. Fig. 3(a) presents AFM image of the film corresponding to normally incident flux, which shows the presence of an ultra smooth surface. On the other hand, AFM images of films deposited at incidence angles of 45° and 87° are shown in Fig. 3(b) and (c), respectively which show granular microstructures. A plot of rms surface roughness (w) versus deposition angle [Fig. 4(a)] shows an increase in roughness at higher deposition angles. For instance, roughness value is lowest for the deposition angle of 0° (0.10 nm) which increases to 0.57 nm for deposition angle of 45°, and reaches up to 1.13 nm for films deposited at 87°. This behavior can be realized as follows. As the deposition angle increases, the shadowing effect becomes more and more prominent to control the columnar morphology. A more accurate assessment of roughness of the films can be obtained from the cross-sectional line profiles [Fig. 4(b)–(d)] obtained from the respective

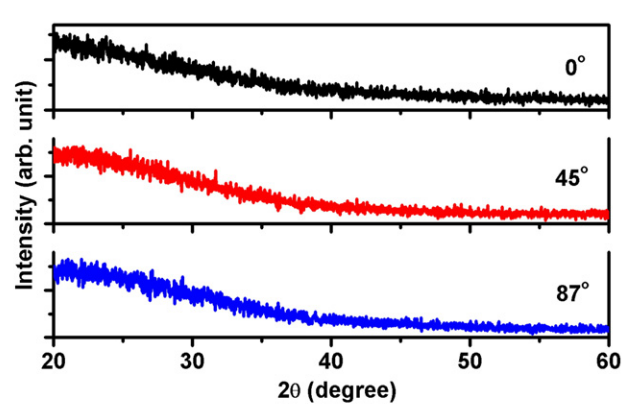

Fig. 1. XRD patterns of TiO_2 thin films sputter deposited at normal as well as oblique incidence.