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Preparation of TiO_2 film by anodisation of sputtered titanium film

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Abstract

Titanium films were prepared on ITO (Indium Tin Oxide) substrate by RF magnetron sputtering. These films were anodized to obtain titanium dioxide thin films. In-order to obtain an optimum thickness for the titanium layer, sputtering was optimized for different sputtering power (100W-150W) and for various sputtering time. The anodisation of Ti film was carried out at room temperature. In this electrochemical process, titanium film was used as anode and platinum as cathode. The electrolytes used were HF solution in aqueous base and NH_4F solution in Ethylene Glycol base. The formation of TiO_2 was strongly influenced by the concentration of the electrolyte, applied voltage and duration of oxidation. The morphology of the oxidized film was analysed using Scanning Electron Microscope (SEM). Evaluation of band-gap supported the formation of Titanium-di-oxide by the process of anodisation of Titanium. The Rutile phase was confirmed using XRD. Resistivity measurement of the titanium films and anodized films of various thickness was carried out using Keithley Source measuring unit. Attempts were made to use this TiO_2 films in Dye Sensitized Solar Cells (DSSC). Though the output of the cell was not appreciable, parameters like short circuit current, open circuit voltage, fill factor and efficiency confirmed the functioning of solar cell.

Key Words: Sputtering, anodization, titanium dioxide, dye sensitized solar cell

Introduction

Titanium dioxide (TiO_2) is one of the most studied metal oxides, which finds many applications in photo catalysis, dye-sensitized solar cells, self-cleaning, electrochemical devices, batteries, gas sensors display, photochromic devices and so forth. Nanostructured form of TiO_2 is currently under intense investigation, as they provide highly active surfaces with a large surface to volume ratio and unique properties[1]. Physical and chemical manipulations in nano dimensions can be applied to enhance/alter the performance of TiO_2 when it is used in the fabrication of micro/nano-size devices for commercial applications[2]. There are many routes for the production of TiO_2nanoforms, of which, one of the most promising routes, even for commercial processes, is anodization. In this method, Ti in the form of a film or foil is anodized in fluoride-ion-containing electrolytes to formTiO_2. In the case of foils it has been reported that by controlling the anodization voltage and time, the dimensions and aspect ratio of TiO_2 can be varied. It also requires optimum concentration of NH_4F and H_2O in the electrolyte [3].

Initial research demonstrated the possibility of forming self-organized, nano tubular surfaces of titanium oxide by anodic oxidation of a Ti foil. Later many groups have conducted comprehensive studies on Ti foil anodization. However, the use of foil limits their potential applications, particularly in the fabrication of microscale devices, where thin films need to be deposited and patterned. Several research groups have developed alternative methods for the fabrication of nanoporous TiO_2 via the anodization of titanium films. One of the earliest studies was conducted by Moret al. who used electrolyte containing acetic acid and hydro-fluoric acid for the anodization of sputtered Ti films. They achieved 20-30 nm diameter nanotube arrays on RF sputtered films at 500°C using a variety of substrates including glass, silicon and alumina[5]. Anodization of thin films is a much less well-known process than foils due to its specific complications. The type of substrate is an important

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factor in the morphological formation and lattice orientation of Ti films. In addition, the deposition temperature, the stress mismatch of the substrate and Ti films, the thickness of the films, and the type of deposition all affect the films which in return affect the anodization process. Different types of fluoride-ion containing electrolytes such as acidic, neutral, aqueous, or non-aqueous electrolytes can be used in the anodization process. Grimes et al. first showed that well-ordered arrays of nanotubes with high surface to volume ratio can be obtained using fluoride-ion-containing neutral non-aqueous electrolytes such as ethylene glycol. There are many other methods for the manipulation of TiO_2 such as the usage of multistep anodization or altering the water content in the electrolyte.

In this work, we have investigated the formation of nanotubes on RF sputtered Ti films on indium tin oxide (ITO) coated substrates[5]. The conductivity and transparency of ITO are the key properties which are utilized in the fabrication of solar cells, displays, optical based chemical and biosensors, as well as many other devices. Knowing how to control the specifications of nanostructured metal oxide films, such as TiO_2 layers, which are formed onto these transparent and conductive substrates, is the key for the successful fabrication of the electro-optical and chromic devices. The formation of nanotubes in Ti films deposited onto ITO glass substrates is worth investigating[6].

Anodization Process

Anodization of titanium occurs as a result of a competition between electrochemical oxide formation and chemical dissolution of oxide by fluoride ions. For anodization, the Ti material should be coated in a conductive slide along with a counter electrode. When there is no F^- ion in the media, a thin barrier metal oxide is formed on the metal surface as

$$Ti+2H_2O \quad TiO_2+4H^+ +4e^-$$

The reaction can be enhanced by the application of an electric field which aids ion transport ($O^{2-}$and Ti^{4+}ions) through the growing oxide. However, as the oxide layer thickness increases in the anodization process, the electric field across the film is progressively reduced. This limits the oxidation process, and eventually the oxidation current (transient current) drops. In this process, Ti^{4+}ions, arriving at the oxide/electrolyte interface, are not made soluble by complexation, and a hydroxide layer (Ti(OH) xOy) precipitates on the surface. This layer is typically loose and porous, and results in further diffusion-retarding effects. In the presence of fluoride ions, the situation is different.

Fluoride ions impose two effects:

(i) They directly complex with the transported cations at the oxide electrolyte interface (thus preventing Ti(OH)xOy precipitation):

$$Ti^{4+}+6F \longrightarrow [TiF6]^2$$

(ii) They also have the ability to react with the oxide to form water-soluble $[TiF6]^{2-}$ complexes (thus, dissolution and breakdown of the barrier layer occurs along a random path through the barrier layer):

$$TiO_2+6F \longrightarrow [TiF6]^{2-} \text{ (dissolution)}$$

This means that the etching will continue, which causes the current to increase at the initial stage. Eventually, the rate of titanium oxide growth (first equation) assisted by electric field equals the rate of dissolution (second and third equations) by fluoride ions, which results in the constant barrier layer thickness. The current eventually decreases due to various effects such as a decrease in the diffusion of fluoride-containing species in and out of the tubes.

Materials and methods

For this study, titanium films of few μm thickness were first deposited onto ITO glass substrates using RF sputtering technique from a 99.99% pure Ti target[5]. RF power of 100-150 W was applied during the deposition process. The deposition time was varied from 1-15 minutes. Hence the film thickness was optimized. The sputtering chamber was pumped down to the background pressure of 10^{-6} torr before introducing the sputtering gas of 100% Ar with a pressure of 10-20 SCCM. The working pressure was about $8^{*}10^{-2}$Torr.

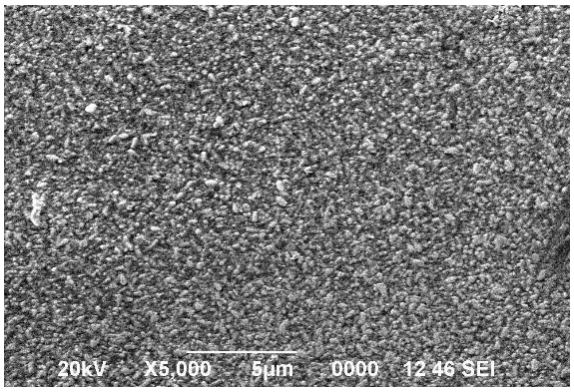

Fig.1 SEM

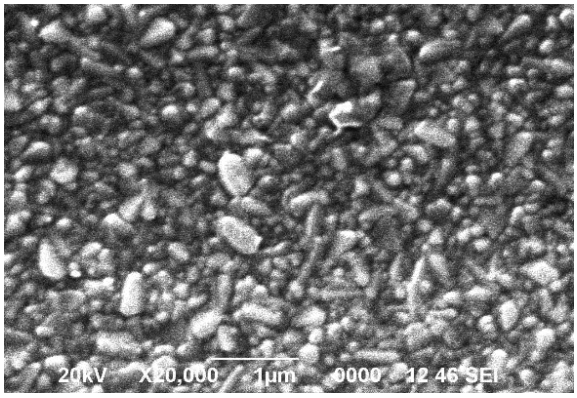

Fig.2 SEM

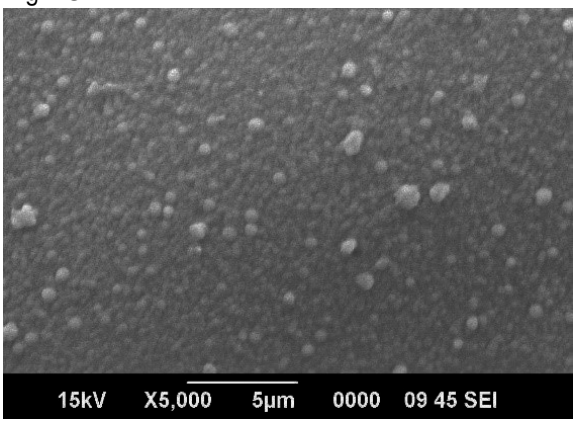

Fig.3 SEM

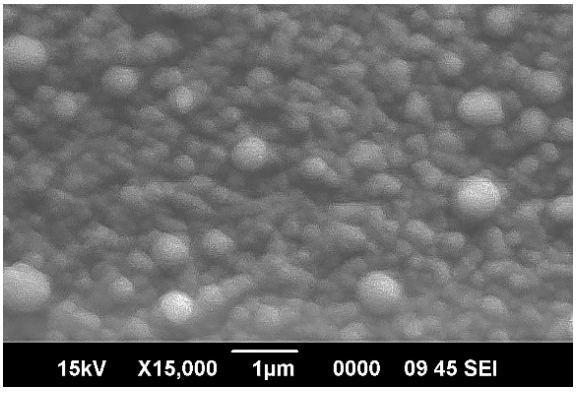

Fig.4 SEM

Anodization was performed in a neutral electrolyte medium of 0.07% (wt) NH_4F/ethylene glycol solution using a platinum wire cathode at room temperature[6]. TiO_2 layers were formed on Ti thin films using anodizing potentials around 1V. The anodizing time was about 30 minutes. Long-term stirring was causing the film to be peeled off during the anodization[7]. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) spectroscopy were employed to determine the surface morphology and the crystalline phase of the TiO_2surface[8]. Using U-V visible spectrophotometer the absorbance and transmittance spectra of Ti and TiO_2 films were studied[9]. The thickness and resistance measurements were appreciable. Resistance of the film was measured using Keithley source measuring unit. As a device application, these TiO_2 films were tried in dye sensitized solar cell (DSSC)[10].

Results and Discussion

Evaluation of surface morphology:

SEM images of the samples are given in Figures 1and 2 under different magnifications.

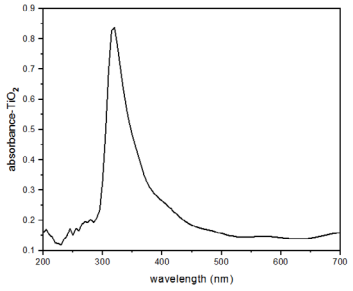

Fig. 5 Absorption spectra

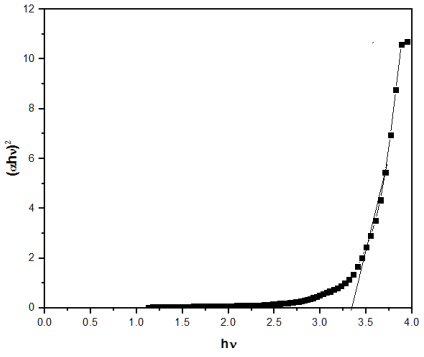

Fig.6 Absorption edge

From these figures, it can be seen that the morphology of the Ti films deposited at room temperature have solid granular deposition.

Figure 3 and 4 shows the morphology of anodized Ti film under different magnification and it can be seen that solid granular nature changes to spherical oxide particles.

Evaluation of optical properties:

From the UV-Vis spectra, figure 5 & 6, the band gap of $TiO_2$was evaluated to be 3.34eV.

X-Ray Analysis

From the XRD pattern shown in figure (7) the rutile phase and crystalline nature of TiO_2 structure was confirmed. Also the average grain size was found to be 3.48A^0.

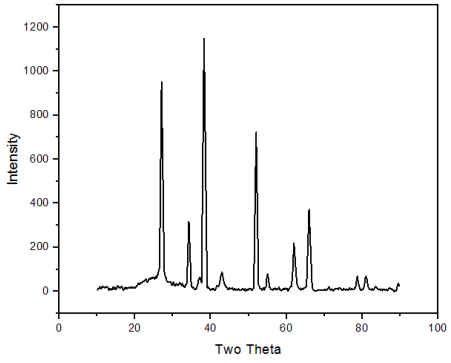

Fig. 7 XRD spectrum of TiO_2

Resistance measurements

Resistance measurements were done using Keithley source measuring unit. In titanium films resistance was found to decrease with increase in thickness, Table 1.

Table .1 Variation of resistance with sputtering time

Sputtered power (Watts)	Sputtered time (minutes)	Measured Resistivity (kilo-ohms per square)
100	1	1.02
100	1.5	0.253
100	2.0	0.118
150	10	0.038

Dye sensitized solar cell (DSSC)

The anodized TiO_2 samples were used for DSSC fabrication. Natural dye from pomegranate was used as sensitizer dye. The V-I characteristics of samples showed output in the power generation quadrant, i.e. the fourth quadrant. This is an appreciable result that hints to the feasibility of a functional solar cell. Here it is to be noted that the order of efficiency of the cell is very poor and it may be attributed to the high series resistance of the TiO_2 layer.

Conclusion

The anodisation parameters play a major role in the formation of well packed uniform layers. Sputtered Ti thin films were anodized by varying the reaction parameters like applied voltage, anodizing time, type of electrolyte and the solution concentration. The surface analysis of the samples was done using SEM and XRD. The best result was obtained for the electrolyte, NH_4F in ethylene glycol base under the optimum solution concentration of 0.07wt%, with an applied voltage of 1 V and the anodizing time of about 20 to 30 minutes. Smooth edged spherical oxide particles were observed in SEM picture.

The band gap of TiO_2 was evaluated to be 3.35 eV. The crystallite size was calculated from the FWHM of the XRD peaks. From the XRD peaks it was concluded that the anodized titanium film resulted in rutile phase. Resistance measurements were done using Keithley source measuring unit. It was found that the resistance of the

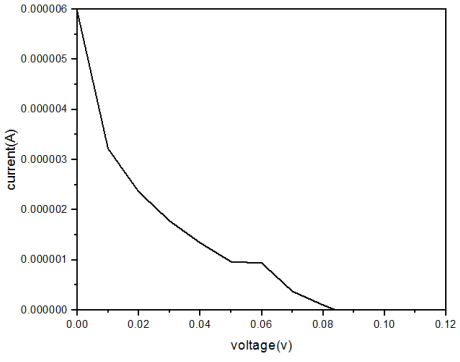

Fig .8 V-I characteristics of DSSC

titanium film decreases with increase in thickness. The resistance of Titanium dioxide film produced by anodisation of sputtered titanium layer was found to be very high. The feasibility of using this TiO_2 film for DSSC fabrication was also tried.

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