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Structural and Morphological Properties of TiO_2 Nanotubes Fabricated *via* Electro-anodization Process

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Abstract

Electro-anodization of thin Ti film deposited on glass substrate by RF sputtering technique was employed to fabricate TiO_2 Nanotubes (TNTs) annealed from 350°C to 650°C. The morphological analysis were done using Scanning Electron Microscopy (SEM), which showed the change in the surface morphology with increase in annealing temperature. The structural analysis was performed using X-ray Diffraction (XRD) and Raman spectroscopy. XRD revealed the presence of anatase phase TiO_2 with most intense anatase peak found at 550°C, at 2θ of 28, 9° (101). Raman revealed the presence of only anatase phase of TiO_2, and showed well-improved crystallinity of the TNTs upon increasing in annealing temperature.

Keywords: Electro-anodization; Fabrication; Annealing; Crystallinity

Introduction

Several techniques used in the preparation of TNTs include sol-gel method [1], hydrothermal method [2], template assisted technique [3] and electrochemical anodization [4]. Electrochemical anodization has been a method of choice to grow ordered nanotubes of controllable pore size and good uniformity and is a cheap and simple technique [4]. The drawbacks of TNTs include the limitation of TNTs by the nature of the substrate, most of the TNTs are grown on metal substrate (e.g. Ti foil). The presence of the metal substrate inhibits application of TNTs in functional micro-devices such as DSSCs and other electrochromic devices that require a transparent metal oxide electrode [5,6]. Some researchers have counteracted the said drawbacks by successfully developed the technology to grow the nanotube arrays from thin titanium films using anodization on a variety of substrates e.g. glass [7,8]. It is of high interest to form nanotube layers from thin Ti films deposited on substrates, such as silicon wafer or glass. In nature, titanium dioxide is found mainly in three polymorphs, anatase, rutile and brookite [9]. The techniques used for depositing titanium films includes evaporation technique, however in this study we used Radio Frequency (RF) sputtering technique.

Experimental Section

Anodization is an electrolytic technique used to develop a passive layer at the anode. Figure 1 shows the schematic diagram of anodizing cell. The electrolyte solution prepared was transferred into electrochemical Teflon cell with titanium film (10 μm) from (Alfa Aesar A Johnson Matthey company) sputter coated glass substrate of dimensions (2 × 2 cm). The substrate was connected to the positive wire of the (PS 8000 T) variable DC power supply using banana plugs (nickel plated brass) purchased from (RS Components) to form an anode electrode and platinum foil (1x1 cm) and (0.025 mm in thickness, 99.9% purity) from (Alfa Aesar A Johnson Matthey company) was connected to the negative wire to form the cathode electrode. The gap between the electrodes was kept constant at 2 cm. Magnetic stirrer was used so as to make sure that the local current is uniform throughout the solution and also to control the viscosity of the solution. The two electrodes attached to the wires using an alligator crocodile clips lead medium. The TRMS Digital Multimeter (C.A 5273) was used to monitor the temperature of the electro-anodization cell and electrolyte throughout the electrochemical anodization process. Electrochemical anodization of glass coated titanium was carried out at 60-100 V for 24-72 hours at ambient temperatures. After 24 hours the DC power supply cooled off by shutting it down for about 3 hours, by so doing preventing overheating or any kind of system breakdown.

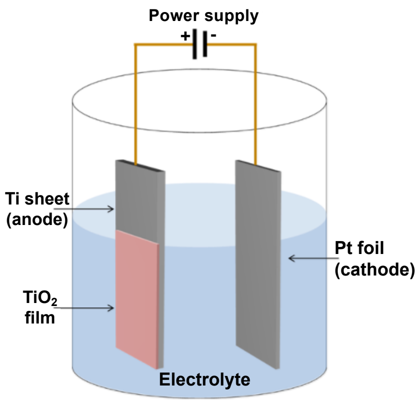

Figure 1: Schematic diagram of anodizing cell.

The anodization was carried out at different voltages ranging from 60-100 V and in each case the voltage was held constant for 12 hours. After the anodization process was done, the as prepared TNTs was again cleaned in ethanol, acetone and subsequently rinse in DI water. The anodised TNTs were allowed to dry in air. Furthermore, the TNTs were then annealed at different temperatures starting from 350°C, 450°C, 550°C, and 650°C. Finally, the prepared and annealed TNTs were characterized using SEM, XRD and CRS.

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Results and Discussions

XRD were performed to obtain the conclusive crystallographic structure and phase properties of TNTs. Figure 2 shows the XRD patterns of the as anodized and annealed titanium dioxide nanotubes grown on functional substrates. At 350°C, the XRD diffractogram in the wide angle range of 2θ (20° < 2θ > 80°) have revealed peaks at 29.43°, 45.10°, 56.52°, 64.92° and 74.81° equivalent to the planes (101), (112), (200), (211) and (204) belonging to a well crystallized anatase phase of TiO_2 (anatase XRD JCPDS Card no. 78-2486) [10]. The emergence of rutile is attributed to the "substrate effect", thus, when the metallic substrate was oxidized, a thin compact rutile layer formed at metal/oxide interface, which initiates anatase to rutile phase transformation [10]. This shows that as the annealing temperature increases, there is an improvement in the crystallinity of the TNTs-FS as the crystalline size decreases. This is in accord with the SEM results showing improved surface morphology of the TNTs-FS as the annealing temperature increases.

Surface and inner morphological characterization of the TNT samples were evaluated using a Scanning Electron Microscopy (SEM). Figure 3 shows Scanning Electron Microscopy (SEM) of TNTs on FTO glass substrate annealed at 650°C. While the structural characterization of titanium dioxide nanotubes was investigated using confocal Raman spectroscopy coupled with Raman imaging. Nature of lattice present, structural make-up of phase, degree of crystallinity, and micro-strain and orientation of crystallites was determined from XRD with incident angles ranging from 20°C to 80°C [11]. SEM was used to characterize the diameter and the length of the tubes along with the structural morphology. SEM provides high resolution images and surface morphology of the sample by focusing electron beam across the surface and detecting backscattered electron signal.

The surface morphology of TNTs (Figure 3(a)) reveals that increasing annealing temperature brings about a slight change in surface morphology of TNTs. The cross sectional view SEM images also revealed smoother TNTs walls as shown in Figure 3(b). The histogram on Figure 3(c) shows that the pore diameter ranges from 125-160 nm, which is smaller than the one observed in 350°C and 450°C annealing temperatures. Figure 3(d) also unveiled a blue area corresponding to the blue spectrum with Raman modes and vibrational frequencies at 156.51 cm^{-1} (E_g), 206.36 cm^{-1} (E_g), 402.57 cm^{-1} (B_{1g}), 520.55 cm^{-1} (A_{1g}) and 638.79 cm^{-1} all belonging to a well crystallized anatase phase of TiO_2.

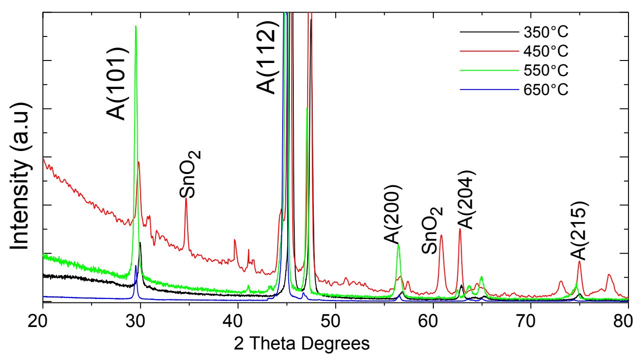

Figure 2: XRD spectra of the anodized TNTs grown on FTO glass substrate prepared at 60 V in NH_4F/glycerol based solution and annealed at 350°C, 450°C, 550°C and 650°C.

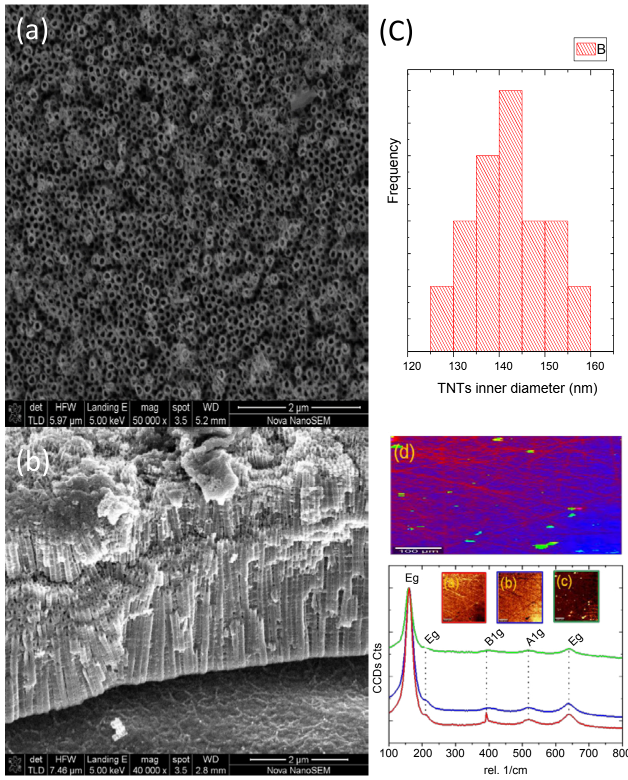

Figure 3: SEM micrographs of TNTs on FTO glass substrate annealed at 650°C (a) Surface SEM images of TNTs, (b) Cross sectional SEM images, (c) Histogram showing pore size distribution and (d) Large area scan of TNTs annealed at 650°C.

Conclusion

Crystalline TiO_2 nanotubes were successfully grown on FTO glass substrate by RF-Sputtering of the Ti films which was then followed by electro-anodization. SEM has revealed that the increase in annealing temperature within a range of 350°C-650°C led to well improved morphology of TiO_2 nanotubes and the pore diameter started to increase. TNTs material grown on FTO glass substrate displayed exceptional stability with no rapturing of the TNTs, unlike other TNTs prepared by other synthetic techniques. The increase in pore diameter of the nanotubes means increased surface area of the nanotubes, which means more loading of the dye, thus more number of photons generated, hence well-improved solar cell performance. XRD analysis of TiO_2 nanotubes confirmed anatase phase. Raman microscopy measurements showed a mutual agreement with SEM and XRD.

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