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Research Article

Synthesis of Titanium Oxide Nanotubes by Anodization Method

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Abstract

In present research work, the prime interest is to grow highly ordered and vertically aligned titanium oxide nanotubes for potential use in the dye-sensitized solar cells. The aim is to achieve high photovoltaic conversion efficiency and low production cost. We have investigated the formation of TiO_2 naonotubes by electrochemical anodization of 25 μm thick and highly pure (99.7%) titanium foil. The electrolyte used is the ethylene glycol with varying concentration of ammonium fluoride (NH_4F) and fixed concentration of deionized water. The nanotubes morphology strongly depends upon applied voltage and fluoride concentration. It is found that double anodization of sample in the same electrolyte results in more ordered structures. So far we have achieved nanotubes with 100 nm diameter and 23 μm long. Scanning electron microscopy and current vs time profile (taken by Lab view software) are used to understand the morphology and growth of tubes. X-Ray diffraction and UV- visible spectroscopy techniques are used for structural information and band gap measurement of semiconductor oxide.

Keywords- TiO_2, nanotubes, anodization, ethylene glycol, NH_4F, Dye-sensitized solar cells.

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1. Introduction

Titanium Oxide (TiO_2) is a famous oxide as compare to other metal oxides as it is highly bio-compatible, inexpensive, chemically stable, non-toxic and having unique semi-conductive properties such as photosensitivity and photoelectrolysis. The later makes it very important in the field of solar cells particularly Dye Sensitized Solar Cells [1,2]. Among the other forms of TiO_2, nanotubes have versatile properties which make them useful in many applications and a topic of today's research [3,4,5,6,7]. These nano tubes are very important for preparation of nano structures as nano rods/ nano wire, etc., and also as photo catalyst, hydrogen generation from water splitting, sensors, transducers, nano capacitor and for the field of solar cells [8,9,10,11]. The research on Titanium Oxide Nanotubes (TNTs) started with the report of Zwilling et al., in 1999 [12]. They had synthesized nanotubular porous structure in acidic fluoride based electrolyte. Later Gong et al. demonstrated the necessary experimental conditions to obtain high-quality and well-ordered TNTs in aqueous dilute HF electrolytes [13]. A great breakthrough in the fabrication of

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TiO_2 nanotubular structure was achieved by Macak et al., and Grimes and group, where they reported very smooth, regular, and very long nanotubes using organic viscous electrolytes [13,14]. Since then different electrolytes like HF, aqueous glycerol, carboxy mythylcellulose aqueous electrolyte and ethylene glycol containing ammonium fluoride (NH_4F) have been successfully used for fabrication of TNTs. Using phosphoric acid and sodium fluoride or hydrofluoric acid, H_2SO_4 as electrolytes for the anodization of titanium has also been reported ([15,16,17,18]. Production of TNTs can be divided in three generations so far. In these three generations, the approximate tube lengths obtained are 500 nm, 7μm, 1000 μm respectively [19]. Third generation for the formation of nanotubes deals with non-aqueous polar organic electrolyte such as ethylene glycol, glycerol, DMSO, etc., containing fluoride ions.

For our study, we have selected the ethylene glycol being nonhazardous, easy to handle and results in better nanostructures. As with the addition of fluoride ions and good selection of voltage, it results in smooth and longer nanotubes with high growth rate. In this research work, we have tried to address the problem of curling and peeling off of oxide layer from the underlying Ti base and introduced a new and easy way of rinsing the oxide with control of temperature as compare to critical point drying as reported by M. Paulause, et.al., [7]. Different methods for the synthesis of TNTs are reported in literature such as hydrothermal synthesis, solgel, photo-electrochemical etching, electrochemical lithography, template assisted fabrication, anodization [20, 21,22,23, 24,25,26]. Among these electrochemical anodization is the method which gives best control of structure. As using this method, we can control voltage, concentration of electrolyte, pH, Temperature and duration and can acquire desired dimensions of tubes. With these unique properties, we have also synthesized our TNTs using electrochemical anodization and studied the effect of voltage change and electrolyte composition. We have also utilized two step anodization method and succeeded in forming open ended nanotubes.

2. Experimental Details

Pretreatment: 99.91% Ti foil with 25 μm thickness was cleaned before anodization. It was sonicated in three different solvents: acetone, ethanol and deionized water in turn for 15 minutes each. After this chemical polishing the surface was very smooth and shiny.

Anodization: After washing in deionized water and drying by blow dryer, electrochemical anodization was performed in ethylene glycol with the addition of deionized water (3 vol %) and ammonium fluoride (0.3 wt% and 0.5 wt%). The electrochemical experiments were performed at three different voltages 40, 50 and 60 volts in two electrode cell with Ti foil as working electrode and lead (Pb) as counter electrode. For each experiment current vs time profile was recorded using Lab View software. All experiments were performed at room temperature and with magnetic stirring.

For double anodization experiments, firstly produced oxide was removed by sonicating in deionized water. The second step anodizing was performed in the same electrolyte composition as of first step anodizing.

Characterization: Scanning electron microscopy, XRD and UV-visible spectroscopy are used to characterize the prepared samples.

3. Results and Discussions

Titanium is a reactive metal. Like other valve metals, it forms a passive layer of oxide on its surface in oxygen containing environment. By sonicating in different solvents, we have tried to remove this naturally occurring oxide and to clean the surface. The two electrode cell experiment in potentiostatic conditions gives a continuous change in current. Change in current with time gives clear information about the growth of nanotubes in three stages.

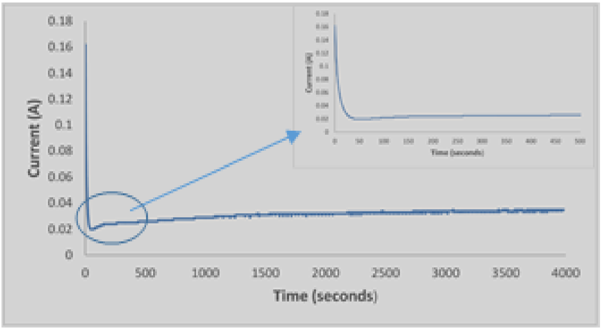

Figure 1. Current versus time profile for anodizing experiment at 60 V and 20 ºC showing the three stages of formation of TNTs.

Fig. 1 shows the current versus time profile for the anodizing experiment at 60V and 20 ºC for a total time of one hour. The information given in the plot is taken by using the Lab View software. This can monitor change in current for every 500 milliseconds. So in one second we can record two values of current. From the figure it is clear that current rises to a high value, decreases and the again increases as usually happens in anodization experiments of metal. The first rise and then decrease show the formation of barrier layer. The next increase shows the formation of pores which then grow in the form of tubes and steady state establishes. During the process of tube formation, two important factors are stress generation and oxide dissolution. Pores or nanotubes forms when a steady state condition establishes between oxide formation and metal dissolution.

Inside the electrolyte the ions present are O^{2-}, H^+, F^-, OH^-. At the metal surface Ti^{4+} are present. As the voltage is applied, these ions get mobile and form an oxide layer on the surface. At the metal surface the chemical reactions are:

$Ti \rightarrow Ti_4^+ + 4e^-$ (1)

$Ti + Ti_4^+ + O^{2-} \rightarrow TiO_2 + 4e^-$ (2)

$2H_2O \rightarrow 4H^+ + 4e^- + O_2$ (3)

$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$ (4)

The above reactions involve movement of O^{2-} and Ti^{4+} ions through the barrier layer. Metal oxide forms at both the interfaces as TiO_2/Ti and TiO_2/ electrolyte interface. To accompany these reactions, hydrogen evolution occurs at the cathode. Fluoride (F^-) ions present inside the electrolyte also move through the barrier type oxide. It reacts with titanium ions at both the interfaces and cause etching of oxide by forming soluble complexes.

$Ti^{4+} + F^- \rightarrow [TiF_6]^{2-}$ (5)

$TiO_2 + 6NH_4F + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O + 6NH_4^+$ (6)

As a result of oxide dissolution and formation of soluble complexes, current rises and go to the steady state conditions. The tube growth occurs with the time depending upon the equilibrium between oxide formation (as in equation 2 and 4) and oxide dissolution (as in equation 6).

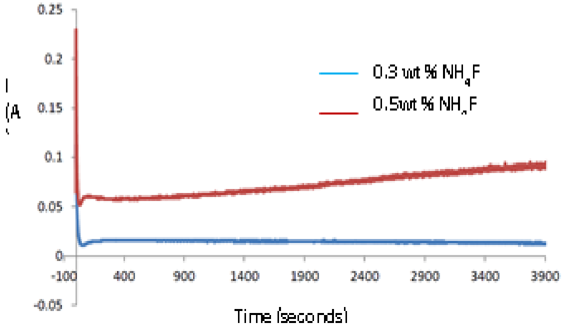

Figure 2. Current versus time profile for anodizing experiment at 60 V and 20 ºC for two different concentrations of NH_4F.

The process of etching is very important for tube growth as more oxide dissolution results in more oxide formation. More concentration of fluoride ions increase this process and more current flows through the electrolyte. This is clearly evident from the Fig. 2, showing the effect of two different concentration of NH_4F for the samples anodized at 60 V. Increasing the concentration of NH_4F from 0.3 wt % to 0.5 wt% has increased the two processes and more current flow. We have done our experiments for maximum duration of two hours and with changing voltages as 40, 50 and 60 volts. With the low voltages as 40 and 50 volts, surface of formed oxide is not clear at all points. Tubes formed were entangled with each other as in the insets of Fig. 3 (a & b).

Very few points show open ends of tubes. In case of 60 V, we have open ended tubes. Also from cross sectional view. It is clear that tubes formed at higher voltages are smoother than those at lower voltages. We concluded that better results are possible with 60 V. With increase in voltage, we have observed increase in length and diameter. We have recorded 100 nm diameter and 17 μm tube length at 60 V. However, with the increase in voltage, we have encountered a problem of peeling off of the oxide layer from the underlying oxide metal. This is due to the difference in thermal expansion coefficient of TiO_2 and titanium metal. Second reason is that fluoride ions move faster through the barrier layer than the oxygen ions. More concentration of fluoride ions at oxide/ metal interface decrease the adherence between the two. We have been succeeded to some extent to overcome the problem of peeling off by giving the thermal treatment to the prepared samples. Since the chemical reactions occurring at the metal surface are all exothermic. The temperature at the surface is higher than the electrolyte temperature. We have rinsed our samples in deionized water at the end by keeping the rinsing bath temperature at few degrees higher than electrolyte temperature. More experiments are required for complete understanding of surface temperature. Since, during the experiment oxide/ metal interface are at high temperature, rinsing at lower temperature produces higher thermal gradient. Reducing the thermal gradient increases the adherence of oxide to the metal.

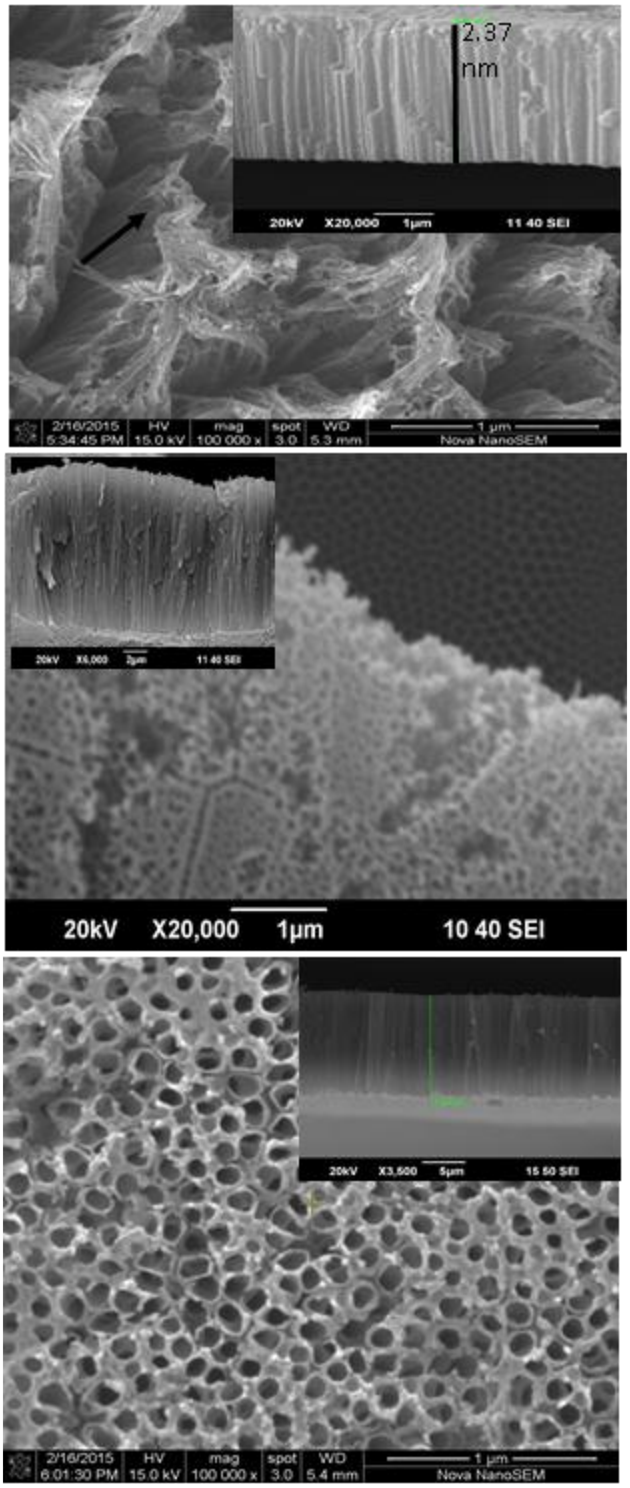

Figure 3. SEM results for first anodizing at a) 40V, b) 50V, c) 60V. Each figure shows the surface of titanium oxide ans in the insets crossectional image.

As indicated by the arrow B in figure 2b, the surface of Ti metal is well patterned by hexagonal arrangements after removal of oxide layer. To utilize this pre-patterned surface, we have performed the double anodization experiments at 60 V. With care of time, we have been able to remove the oxide layer by just sonicating the samples in deionized water. We have found many interesting results as Figure 4. Surface of oxide is very clear. No debris are present on it. Tubes are highly ordered and open ended. There is no need to use special chemical or mechanical treatment to open the pores.

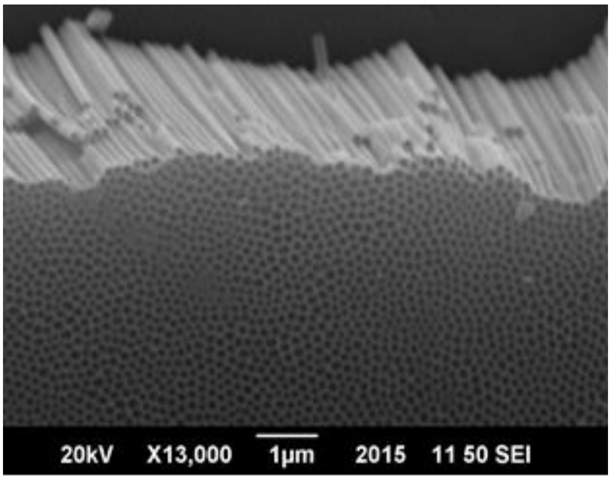

Figure 4. SEM results for double anodization at 60V showing the surface and cross section of TNTs. Inset shows the highly ordered nanotubes surface.

The cross-sectional image shows that tubes are very smooth and aligned. Higher magnification image clearly indicates that tube diameter is constant and not varying as in the case of single anodization.

The as produced TNTs were amorphous. To produce crystalline TNTs we have performed annealing of tubes at different temperatures as 400°C, 450°C, 500°C and 550°C for six hours with heating rate of 5°C/min.

Samples used for this study were anodized under same conditions for two hours at 40 volts with 0.5 wt% NH_4F. X-Ray diffraction analysis was carried out to examine the crystallinity induced in the samples. Two phases' rutile and anatase were present. As anodized samples were amorphous but annealed samples show sufficient crystallinity and a highest peak at 44° (2-theta) of Rutile (210) plane was observed. This depicts that the structure has a texture and (210) is the preferred orientation along which most of the crystallization has occurred. Second highest peak was of anatase (101) plane at 27° 2-theta. The result shows that anatase phase increases with increasing the temperature up to 500 ºC.

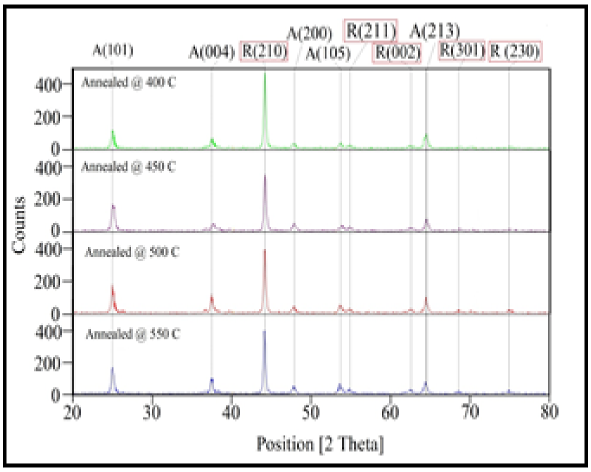

Figure 5. XRD plot of Pure titanium, as anodized nanotubes on titanium and nanotubes annealed at different temperatures without Ti-Substrate.

4. Conclusions

The study of TNTs by electrochemical anodization method reveals that high voltage as 60 V gives open ended and smooth tubes. These results become much more pronounced with the double anodization experiments. There is no need of chemical or mechanical treatment for opening the top ends of tubes. Highly regular patterened tubes can be obtained. Thermal treatment during rinsing the sample can decrease the temperature gradient at the surface or interface (TiO_2/ Ti) and improves the adherence. More experiments are required to understand the surface temperature. XRD data shows that upto

500 ºC, anatase phase percentage in the crystalline phase of TNTs could be increased. Increasing more temperature decreases this percentage.

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