Electrochemical Anodization and Characterization of Titanium Oxide Nanotubes for Photo Electrochemical Cells

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Abstract. Due to its multitude of applications, titanium oxide is one of the most coveted and most sought-after materials. The above experiment demonstrated that TiO₂ nanotube arrays might be formed by electrochemical anodization of titanium foil. The 0.25 wt% ammonium fluoride (NH₄F) was added to a solution of 99% ethylene glycol. Anodization is carried out at a constant DC voltage of 12V for 1 hour. Then, the annealing process is carried out for 1 hour at 480°C, which is known as an annealing. FE-SEM were utilized to evaluate the surface morphology of the nanotube arrays that were made. At the wavelength of 405 nm, sharply peaked photoluminescence intensity was observed, which corresponded to the band gap energy (3.2 eV) of the anatase TiO₂ phase. Since free excitations appear at 391 and 496 nm, and since oxygen vacancies are developed on the surface of titania nanotube arrays, it is reasonable to conclude that free excitations and oxygen vacancies are the causes of humps at 391 and 496 nm, and that they may also be present at 412 and 450 nm. FESEM results showed uniformly aligned TiO₂ nanotube arrays with an inner diameter of 100 nm and a wall thickness of 50 nm

Keywords: Titanium oxide nanotube arrays, Electrochemical Anodization, Photoluminescence, X-ray Diffraction, Bandgap, Field Emission Scanning Electron Microscope.

1. INTRODUCTION

Today, it is necessary to employ a wide variety of materials in order to design and create gadgets which are currently acceptable for a number of commercial applications. The increased demand for nanomaterials has led to increased interest in current technologies that build high-performance circuits. Geometry, shape, and morphology of nanostructures all have a crucial role in determining the effectiveness of nanostructures [1]. When increased understanding of nanoscale materials will be implemented, a better integration of theory and models will lead to previously unthought-of advancements in predicting and designing material properties at all scales ranging from atomic-molecular nanostructure to microstructure behavior. This will lead to previously unseen levels of advancement in the prediction and design of materials properties. The fact that titanium dioxide nanotubes (TNT) have lower production costs, a larger surface-to-volume ratio,
and a better combination of attributes has fueled their increase in popularity as a result of their use in various nanostructured oxide materials. Because of the diverse applications in which TNT has been used, there have been a variety of applications considered for TNT, including pool boiling [4, 5–10], photocatalysis [11–12], hydrogen generation [13, 14], corrosion resistance [15], solar cells [16–17], sensors [18, 19], storage device [20], and catalyst support [21]. In comparison to conventional anodization, electrochemical anodization offers the best capabilities, such as the ability to establish a specific thickness and size for the resulting nanotube arrays with the desired dimensions. It is also capable of providing specializations tailored to specific applications with its uniform, controllable process, and is advantageous when performing electrochemical anodization as compared to the other options. This process is also a cost-effective one, and the tubes formed in this manner have a very strong adhesive strength. Also, the anodization variables make it possible to change the film thickness and form simply by increasing or decreasing the value of the variable.

2. EXPERIMENTAL METHOD

Electrochemical anodic oxidation was used to create the TiO2 nanotube array film. Sigma- Aldrich, Bangalore, provided a high purity titanium (99.8%) plate with a thickness of 0.25 mm, which was washed in DD water and then rinsed with acetone for 10 minutes. In a cylindrical electrochemical reactor, TiO2 nanotube arrays were created. The experimental setup includes an anode as the working electrode and Platinum Pt as the co-electrode (cathode) immersed in an electrolytic solution of 0.25wt% ammonium fluoride (NH4F) dissolved in 99 percent ethylene glycol. Anodization is carried out at a continuous DC voltage of 12V for 1 hour at a certain anodization time and then annealed at 4800C for 1 hour. The electrolytic solution employed has a pH of 4.3 and a mortality of 0.06M.

![Experimental setup of Electrochemical Anodization](image)

Opposing processes occur at the oxide/electrolyte interface, with one being the hydrolysis of TiO2 and the other being the dissolution of TiO2. The TiO2 nanostructures formed are dependent on which of these two processes is happening at the oxide/electrolyte interface [24, 25]. To anodize fluorides present in the electrolyte, the two procedures result in the creation of vertically aligned titanium oxide nanotubes on the surface of titanium substrates (mixture of ammonium fluoride and ethylene glycol).

3. MEASUREMENTS

High-resolution surface images were acquired by employing (FEG-SEM). By employing an XPERT-PRO X-ray diffractometer with Cu K radiation (\(\lambda = 1.54060 \text{ Å}\)), the structure and crystalline nature of titania nanotubes were investigated. The bandgap energy was determined using a Photoluminescence (PL)
spectrum obtained with a Photoluminescence Spectrometer at an excitation wavelength of 320nm.

3.1. FEGSEM Analysis

The two figures displayed in this section provide a top view of the TiO2 nanotube array surface structure in FEG-SEM at a magnification of 700KX and 400KX, respectively. When using the self-organized Nano porous TiO2 tubes, it was discovered that the resulting tubes had a length of 200 nm, a pore width of 100 nm, and a wall thickness of 50 nm.

Figure 2. Image of the sample anodized for 1 hour at 12V potential at 700.00 KX magnification.

Figure 3. Image of the sample anodized for 1 hour at 12V potential at 4.00 KX magnification.

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3.2. XRD Analysis

The x-ray diffraction pattern of TiO2 nanotube arrays recorded in the range of 10°-90°. The values of 2θ, d-spacing, relative intensity and FWHM are obtained from the XRD pattern. The low intensity peaks at 2θ values of 36.24°, 62.08°, 76.56°, 79.71° and 82.40° are corresponding to the anatase phase. It has been reported that the remarkable broad peaks in the XRD pattern confirm the existence of amorphous phase
[26, 27]. However, the other peaks at 2θ value of 39.54°, 41.31°, 54.13° and 72.40° are related to the titanium substrate itself. The obtained peaks in XRD pattern are consistent with JCPDS Card No. 021-1272.

![Figure 4. X-ray diffraction pattern of anodic TiO$_2$ nanotube arrays annealed at 480 °C for 1 hour](image)

**Table 1.** XRD parameters of anodic TiO$_2$ nanotube arrays annealed at 480 °C for 1 hour

| S.No | 2θ (degree) | Intensity (counts) | $d_{observed}$ (Å) | $d_{jcpds}$ (Å) | FWHM (degree) | Planes |
|------|-------------|--------------------|---------------------|-----------------|---------------|--------|
| 1    | 36.24       | 433.0              | 2.48                | 2.54            | 0.14          | (101)  |
| 2    | 39.54       | 294.0              | 2.33                | 2.29            | 0.16          | (200)  |
| 3    | 41.31       | 222.0              | 2.23                | 2.18            | 0.12          | (111)  |
| 4    | 54.13       | 151.0              | 1.71                | 1.68            | 0.12          | (211)  |
| 5    | 62.08       | 109.0              | 1.47                | 1.47            | 0.12          | (002)  |
| 6    | 72.40       | 102.0              | 1.33                | 1.30            | 0.12          | (311)  |
| 7    | 76.56       | 400.0              | 1.24                | 1.24            | 0.10          | (202)  |
| 8    | 79.71       | 58.0               | 1.22                | 1.20            | 0.10          | (212)  |
| 9    | 82.40       | 411.0              | 1.17                | 1.17            | 0.08          | (321)  |
3.3. PHOTOLUMINESCENCE SPECTROSCOPY

To fabricate and analyze self-aligned TiO2 nanotube arrays, the TiO2 nanotube arrays are generated using potentiostatic anodization of two different electrode topologies. The image presented in Figure 5 displays the photoluminescence (PL) emission spectra of TiO2 nanotubes arrayed on titanium foil in the wavelength range of 300-600nm at ambient temperature. A significant PL emission peak is observed at 405 nm, which is associated with the band gap energy (3.1eV). The bulk anatase TiO2 phase has a band gap energy of 3.2 eV. The oxygen vacancies that may have developed on the surface of titania nanotube arrays at 412 nm and 450 nm might be explained by a little protrusion at 412 nm and 450 nm, which may be indicative of oxygen vacancies. One more hump was observed in the form of two wavelengths of 496 nm and 391 nm, which may indicate free excitations.

4. CONCLUSION

Anodic oxidation of TiO2 has been used to make nanotube arrays, which have since been characterized. When considering the band gap energy of the bulk TiO2 anatase phase, the group peak about 405 nm in the PL emission spectrum is clearly present. Also, a number of small humps were also observed in PL spectra, which could be attributed to free excitations or the production of oxygen vacancies on the surface of titania nanotube arrays. A natural test that validates the anatase phase of TiO2 nanotube arrays is by measuring the XRD, and the peaks seen in the XRD pattern are in agreement with JCPDS Card No. 021-1272. FESEM (Focused Electron Scanning Electron Microscope) has verified the existence of nanotube arrays with an inner diameter of 100 nm and a wall thickness of 50 nm. With regard to the anatase TiO2 nanotube arrays that have been manufactured, they are appropriately aligned and hence acceptable for use in Photo Electrochemical Cells for Hydrogen Generation.

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