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EFFECTS OF SYNTHESIS PARAMETERS ON THE STRUCTURE OF TITANIA NANOTUBES

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Abstract

Detection of hydrogen is crucial for industrial process control and medical applications where presence of hydrogen in breath indicates different type of health problems particularly in infants. A better performed sensor with high sensitivity, selectivity, reliability and faster response time would be critical and sought after especially for medical applications. Titanium dioxide nanotube structure is chosen as an active component in the gas sensor because of its highly sensitive electrical resistance to hydrogen over a wide range of concentrations. The objective of the work is to investigate the effect of the anodizing conditions on the structure of titania nanotubes produced by anodizing method. The anodizing parameters namely the ambient temperature and separation of electrodes are varied accordingly to find the optimum anodizing conditions for production of good quality titania nanotubes for enhanced properties based on their uniformity, coverage, pore size and crystallinity. Samples of nanotubes produced were subjected to annealing process at varying time and temperature in order to improve the crystallinity of the nanotubes. The highly ordered porous titania nanotubes produced by this method are of tabular shape and have good uniformity and alignment over large areas. The pore size of the titania nanotubes ranges from 47 to 94 nm, while the wall thickness is in the range of 17 to 26 nm. The length of the nanotubes was found to be about 280 nm. The structure of nanotubes changes from amorphous to crystalline after undergoing annealing treatment. Nanotubes have also shown to have better crystallinity if they were subjected to annealing treatment at higher temperature. The characteristics of nanotubes obtained are found to be agreeable to those that have been reported to show improved hydrogen gas sensing properties.

Keywords: Anodization, Titania, Nanotubes, Hydrogen, Gas Sensor

1. Introduction

There is a great demand for accurate detection of molecular hydrogen (H_2) for various applications in industrial process such as in chemical and petroleum refining, production of high purity gases in semiconductor industry and production of krypton, xenon and neon for the lighting industry, where hydrogen is a contaminant that must be quantified to certain range of levels.

Clinically, breath hydrogen is considered to be an important and relevant parameter for detection of lactose intolerance [1], fructose malabsorption [2], diabetic gastroparesis [3], and neonatal necrotizing enterocolitis [4]. The hydrogen concentration present in the exhaled gas will indicate the different type of health problems respectively.

Titania nanotubes are believed to work very well as gas sensor in terms of the sensitivity and response especially towards hydrogen. Varghese et al [5] have carried out research to study what factors affect the sensitivity of hydrogen sensors using titania nanotubes. It is also found that titania nanotubes demonstrate photocatalytic and photoelectrochemical properties [6].

There are a few methods developed by other researchers to produce titania nanotubes like soft chemical process [7] and deposition of titania onto alumina template [8]. However, the anodization technique is found to be the easiest and simplest method to date as compared to other methods because it is a simple and fast procedure. It also allows good control over the pore size and the uniformity of the nanotubes at low cost. Anodization is the process of oxide growth when a material is submerged in an electrolyte and is biased anodically with respect to a counter electrode. The highly ordered porous titania nanotubes produced by this method have good uniformity, controllable pore size and in the amorphous state. The anodizing parameters and conditions are very crucial in order to obtain the titania films in the form of nanotubes. As these parameters [7, 9] will determine the tube-like structure of the nanotubes and also the length, diameter and wall thickness of the tubes.

Titania nanotubes fabricated using anodization technique [6, 9, 10] will have large surface areas and high reactivities. Due to the chemisorption of the dissociated hydrogen on the titania surface, the electrical resistance of the titania nanotubes is highly selective to hydrogen over a wide range of concentrations. During chemisorption, hydrogen acts as a surface state and a partial charge transfer takes place from hydrogen to the conduction band of titania. This creates an electron accumulation layer on the nanotube surface that enhances its electrical conductance. When the hydrogen ambient is being removed, electron transfer takes place back to hydrogen and it desorbs, thus the original resistance of the nanotubes is restored. It is believed that the sensitivity to hydrogen is highly dependant on the diameter of the nanotubes, with the smaller ones being much more sensitive, possibly of about several hundred times greater. However, smaller diameter nanotubes tend to be more brittle and harder to handle without breaking [5].

Post-treatment such as annealing process in oxygen ambient is important in order to transform the structure of titania nanotubes produced from amorphous to crystalline [6]. The crystalline structure was reported [11] to be critical for gas sensing. This structure allows diffusing hydrogen atoms to easily accommodate the interstitial sites [12, 13] of titania nanotubes, hence increasing the sensitivity of titania nanotubes towards hydrogen. Higher annealing temperature is believed to increase the crystallinity, but the nanotubes will collapse if the temperature is too high (> 580ºC) [5]. This is due to the oxidation of the underlying surface of titanium substrate that results in the amorphous oxide layer which will disrupt the nanotubes structure.

Therefore, the objective of this work is to study the synthesis parameters namely electrode separation and ambient temperature of anodization method to produce titania nanotubes with desired characteristics believed to be suitable for hydrogen sensing applications. The effect of the post-treatment, oxygen annealing process on the produced titania nanotubes is also investigated.

2. Experimental Methods

Titanium foil with purity of 99.6 % and thickness of 0.25 mm is cut out into 7x15 mm² dimension. The anodization is performed in an electrolyte medium of hydrofluoric acid in water, using platinum foil cathode with 99.99 % purity. The anode and cathode have the same dimension. The anodization set-up is shown in Fig. 1.

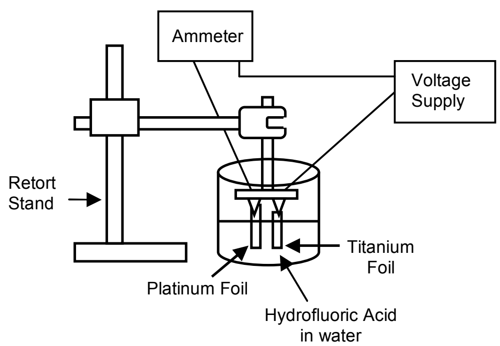

Fig. 1. Anodization Set-up.

The anodizing voltage was set at 20 V using direct current power supply and the electrolyte was 0.5 vol % hydrofluoric acid in water. The volume of the electrolyte used for anodization is 100 cm^3. The anodization time is 20 minutes. These anodizing parameters (voltage, concentration of electrolyte, and duration) were set at conditions where other researchers [6, 10, 14, 15] find it regularly successful in producing the titania nanotubes. Platinum and titanium electrode are placed face to face in parallel at separation of 7 cm and 2 cm with ambient temperature ranging from 23°C to 29°C. Magnetic stirrer was used during anodization process in order to improve the uniformity of nanotubes.

Annealing process was carried out in pure oxygen. Two samples were annealed at 470ºC for 4 and 6 hours respectively and another two samples were annealed at 500ºC and 530ºC for 4 hours respectively. The heating and cooling rate was set at 1ºC/min to avoid thermal induced stress to the sample. Field emission scanning electron microscope (FESEM-LEO model 1525) was used to study the surface morphology of the samples produced. X-Ray diffractometer (XRD-Bruker) was used to determine the crystalline phase.

3. Results and Discussion

Figures 2 and 3 show the FESEM images of the surface structure of titania nanotubes produced before and after annealing process respectively. This sample is produced by using magnetic stirrer at ambient temperature of 23°C and a separation between titanium and platinum electrodes of 2 cm.

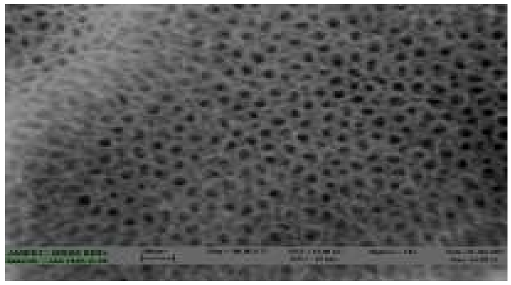

Fig. 2. Titania Nanotubes before Annealing.

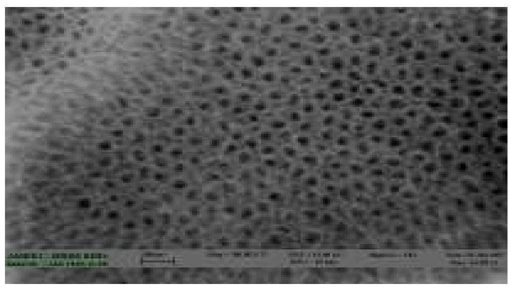

Fig. 3. Titania Nanotubes after Annealing.

After annealing, it can be observed that the physical structure remains the same. The observed structure is similar to the structure obtained by Gong [6]. The diameter of the tubes ranges from 47 nm to 82 nm. The average diameter for the tubes is 67 nm and the average wall thickness is 17 nm. Fig. 4 shows the side view of the titania nanotubes and also the bottom of the nanotubes. The length of the nanotubes for this sample is about 280 nm. The coverage and uniformity of the honeycomb structure of titania nanotubes fabricated is shown in Fig. 5.

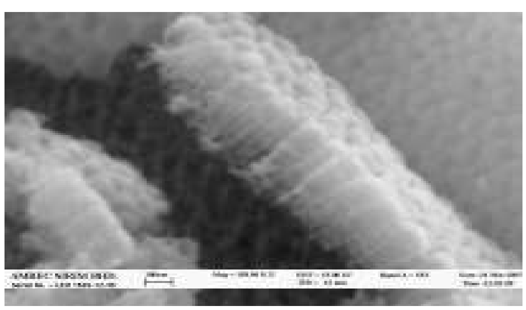

Fig. 4. Cross-Sectional View of Nanotubes.

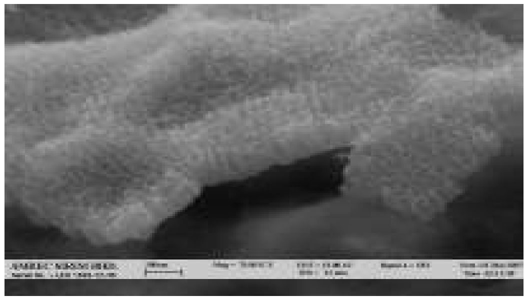

Fig. 5. Coverage and Uniformity of Nanotubes.

Figure 6 shows the surface structure for the sample anodized with separation between titanium and platinum electrodes at 7 cm while Fig. 7 shows the sample produced at room temperature of 29°C. The other anodizing parameters remain the same for each sample.

The structure observed in Fig. 6 is similar to the structure obtained by Gong [6] during the oxidation stage. The surface is covered with uneven oxide layer and thus no formation of nanotubes can be observed. This shows that the increment in the separation distance between the titanium foil anode and platinum foil cathode may have causes only small amounts of titanium ions that can be mobilize and migrate since the electric field is not strong enough due to the distance of separation.

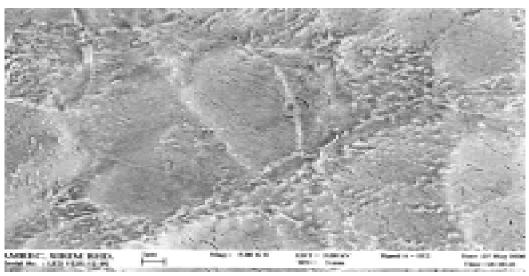

Fig. 6. Anodized Titanium at 7 cm.

The higher room temperature also did not produce nanotubes as observed in Fig. 7. The oxide layer has been obtained but the well-aligned tubes like structures are not acquired. This shows that lower temperature is needed to produce the porous structure of the nanotubes [15]. Elevated electrolyte temperature may increase the dissolution speed of titania making it too fast to form either porous or nanotubes structure as have been observed by anodized Aluminium [16].

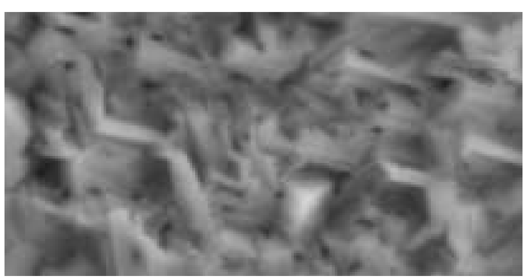

Fig. 7. Anodized Titanium at Room Electrode Separation Temperature of 29°C.

The XRD spectrum in Fig. 8 shows the amorphous structure of the nanotubes before annealing without any obvious crystallite peak observed.

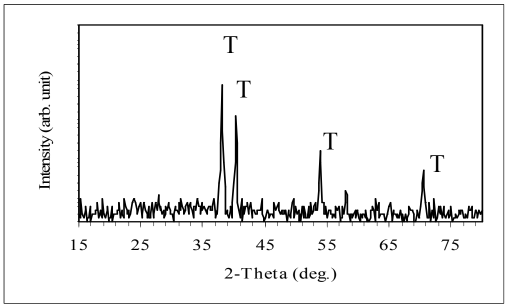

Fig. 8. X-ray Diffraction Pattern of Nanotubes before Annealing. T Represents the Reflections from Titanium Substrate.

Figure 9 shows XRD spectra of nanotubes annealed in different annealing time. Both spectra confirm a crystalline structure in the titania nanotubes film. However, the sample annealed for 6 hours has higher intensity at the peaks than the sample annealed for 4 hours. This result suggests that the crystallinity of the tubes improved with longer annealing time. It can be seen that anatase phase of titania is present in both sample but rutile phase is only present in nanotubes annealed at temperature higher than 470ºC as observed in Fig. 10. At annealing temperature of 500ºC and 530ºC, XRD spectra shows the reflections of anatase and rutile crystallites.

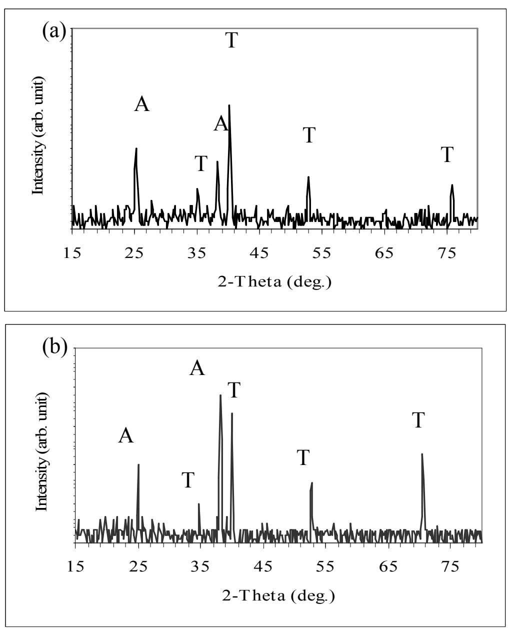

Fig. 9. X-ray Diffraction Pattern of Titania Nanotubes Annealed at 470ºC for (a) 4 Hours (b) 6 Hours. A and T represent the Reflections from Anatase Crystallites and Titanium Substrate Respectively.

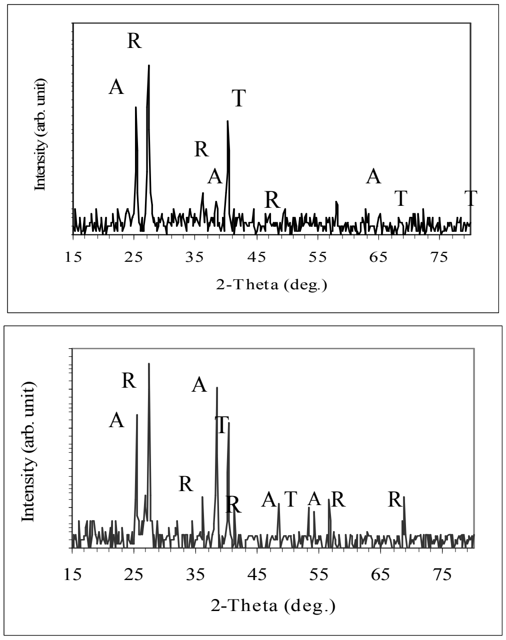

Fig. 10. X-ray Diffraction Pattern of Titania Nanotubes Annealed at (a) 500ºC (b) 530ºC for 4 hours. A, R, and T Represent the Reflections from Anatase Crystallites, Rutile Crystallites, and Titanium Substrate Respectively.

The sample annealed at 530ºC has higher intensity at the peaks and is better crystallized than the sample annealed at 500ºC and 470°C. Therefore, higher annealing temperature is believed to improve the crystallinity of the nanotubes. The anatase structure has been reported to be highly sensitive towards hydrogen [12, 17, 18] and have higher contribution to hydrogen sensitivity as compared to rutile due to higher c/a ratio. The higher c/a ratio enables the anatase lattice to accommodate the diffusing hydrogen atoms easily [12, 13]. Varghese et al [5] have found that the anatase crystallites were concentrated on the wall of the nanotubes and rutile at the bottom of the tubes.

4. Conclusions

The anodization technique has been used to fabricate aligned titania nanotubes. The anodizing parameters and conditions are very crucial in getting the nanotubes structure. From the investigation, anodization of titanium carried out at 20 V in 0.5 vol % hydrofluoric acid in water with electrode separation of 2 cm at ambient temperature of 23°C have been found to produce good quality titania nanotubes.

The quality of the nanotubes is based on the uniformity, good coverage and range of the pore size required for gas sensing applications as reported by Varghese et al [5]. Diameter of the nanotubes produced ranges from 47 nm to 82 nm and the average wall thickness is 17 nm. The length of the nanotubes is about 280 nm. Annealing in oxygen ambient is found to be an important post-treatment process to transform the titania nanotubes from amorphous to crystalline structure. Higher annealing temperature and longer annealing time is believed to produce better crystalline structure as shown by the XRD spectra. Both anatase and rutile phase of titania are present in nanotubes subjected to annealing process at 500°C and 530°C. The optimum annealing temperature for titania nanotubes at the moment is 530ºC.

Acknowledgements

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