

Growth of TiO₂ Nanorods by HFCVD

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Abstract

The aim of this research is demonstrating the growth of titanium oxide Nano-rods. In our testing, growth of nano-rods was achieved using the Hot Filament Chemical Vapor Deposition (HFCVD) method. We studied the effects of temperature and time on the growth of nano-rods. We also investigated the effect of Co catalyst on the growth of nano-rods so that we would be able to measure the titanium content in different times and temperatures. Our samples were studied using Scanning Electron Microscopy (SEM) , Raman Spectroscopy, EDX, and Dot mapping, XRD.

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1. Introduction

Titanium was once considered a rare metal, but nowadays it is one of the most important metals in the industry. The element was first discovered in England by Gregor in 1790, although it did not receive its name until Klaproth named it after the mythological first sons of the earth, the Titans, in 1795. Chemically, titanium is one of the transition elements in group IV and period 4 of Mendeleef's periodic table. It has an atomic number of 22 and an atomic weight of 47.9. Being a transition element, titanium has an incompletely filled d shell in its electronic structure.[1] Oxygen is a common element introduced into metals to modify their mechanical, physical, chemical, and biological properties using either conventional beam-line ion implantation or PIII. A number of papers have reported that the wear resistance, corrosion resistance, and biocompatibility of titanium and its alloys can be improved by oxygen membranes (AAMs), organogel and supramolecular template. However, one of the limitation of this technique is a weak driving force and low solid content. In order to overcome this shortcoming,

implantation. Titanium oxide is known to have varying stoichiometries and the common compounds are Ti₃O to Ti₂O, Ti₃O₂, TiO, Ti₂O₃, Ti₃O₅ and TiO₂ . [2] Titanium dioxide, TiO₂, is of great research interest for various applications including photo catalysis [3–5], solar cells [6], sensors [7], lithium batteries [8], antimicrobial activity [9] as well as self-cleaning and antifogging. [10,11] Nano-sized materials have attracted growing interest due to their unique structure and properties. Much work has recently concentrated on the important metal oxides, such as TiO₂, V₂O₅, Al₂O₃, ZnO, SiO₂ and WO₃ which are generally characterized with catalytic behaviors, size quantization effects, nonlinear optical properties, unusual luminescence, etc. [12–16] the sol-gel template method has been reported to synthesize TiO₂ nanotubes, nanorods and nanowires from the anodic alumina Limmer et al. [17,18] reported the electrophoretic deposition method, which applied an electric power between an anode of Pt mesh and an aluminum cathode for leading the charged solid particles

mobility. This electrophoretic method allows to fabricate large areas of uniformly sized nanorods with desired patterns. Nevertheless, most of the oxide

2. Experimental set-up

In this project, We first cut a silicon wafer with an original diameter of 20 cm into 1cm × 1cm pieces clean the pieces using aston(C_3H_6O), etanol(C_2H_6O) and DI water in an ultrasonic cleaner, and then deposit layer of Co (as catalyst) on the Si substrate using a Plasma Enhanced Chemical Vapor These condition will result in perforation of the surfaces and creation of the needed sites over the catalyst film. After the surfaces are primed and the catalyst layer is set, TiO_2 nanostructures are cultivated using a Hot Filament Chemical Vapor Deposition (HFCVD) device. The Si substrate (which is coated with Co catalyst) is placed up on the heater surface and the system is sealed so that the inside can be vacuumed using rotary pump and diffusion. An initial vacuum of 10^{-3} torr should be achieved before the samples are etched, which is done before the outset of the actual growth stage. Here, NH_3 and H_2 gases are used for etching in the manner explained below. H_2 with a flow of 48.4 sccm and NH_3 with a flow of 48.4 sccm are injected into the chamber. Pressure is set to 5 torr and then the temperature is adjusted to 567 °C. A voltage of 5V and a current of 13.5A are applied. NH_3 and H_2 molecules hit the heated filament and then the catalyst surface and the etching is thus achieved. This operation takes 10 min and is followed by the actual growth stage. At this stage, TTIP (titanium tetra isopropoxide) is used as the precursor and Ar as the carrier gas and extenuator. After etching is completed, Ar with a sccm and current is set at 13.3 A. The SEM picture has a resolution of 1um and it shows that titanium dioxide nanorods have a length of 821.38 nm and a diameter of 262.06nm. Fig2 a shows the Raman

sol solutions have low electric conductivity, so they need to adjust the pH value by introducing acid in an electrophoretic deposition method. [19]

Deposition (PECVD) device. In this work, before the growth of TiO_2 nanorods begins in each test, operation is conducted. Gases used for etching are H_2 and NH_3 , which are injected into the reaction chamber, ionized into free radicals by a heated filament, and are brought in contact with the surfaces. flow of 63.2sccm is injected into the TTIP chamber. It comes in contact with TTIP and is heated, along with the other vapors, to 650°C. It is then mixed with NH_3 vapor with a flow of 63.2sccm and the mixture is injected into the reaction chamber of the Hot Filament Chemical Vapor Deposition (HFCVD) device. After completion of the growth stage, Ar/ NH_3 and TTIP gas flows are stopped and the filament and the system as a whole is left to cool. Eventually, and after the device is cool enough and the vacuum seal broken, the sample are taken out of the chamber and transferred to analysis centers to undergo SEM, Raman, EDX, Dot mapping.

3 .Results and discussion

Fig 1 shows the SEM results. Fig a shows the result at 15min and a pressure of 1 torr, Ar and NH_3 flow being 63.2sccm, voltage and current and temperature being set at 5v, 13A, and 567 °C respectively. At this temperature the Co surface is graying, with measured sizes of grains being 124.06, 97.94 and 108.85 nm. Fig b depicts a situation where, at 30min time, the pressure and temperature are 1 torr and 650 °C respectively. Ar and NH_3 gas flow is 63.2 spectrometry at 30 min and 650 °C. At 650°C, 490,509,558,613,787 cm^{-1} peaks are generated by Anatase phase while 435 cm^{-1} peaks are generated by Rutile phase.

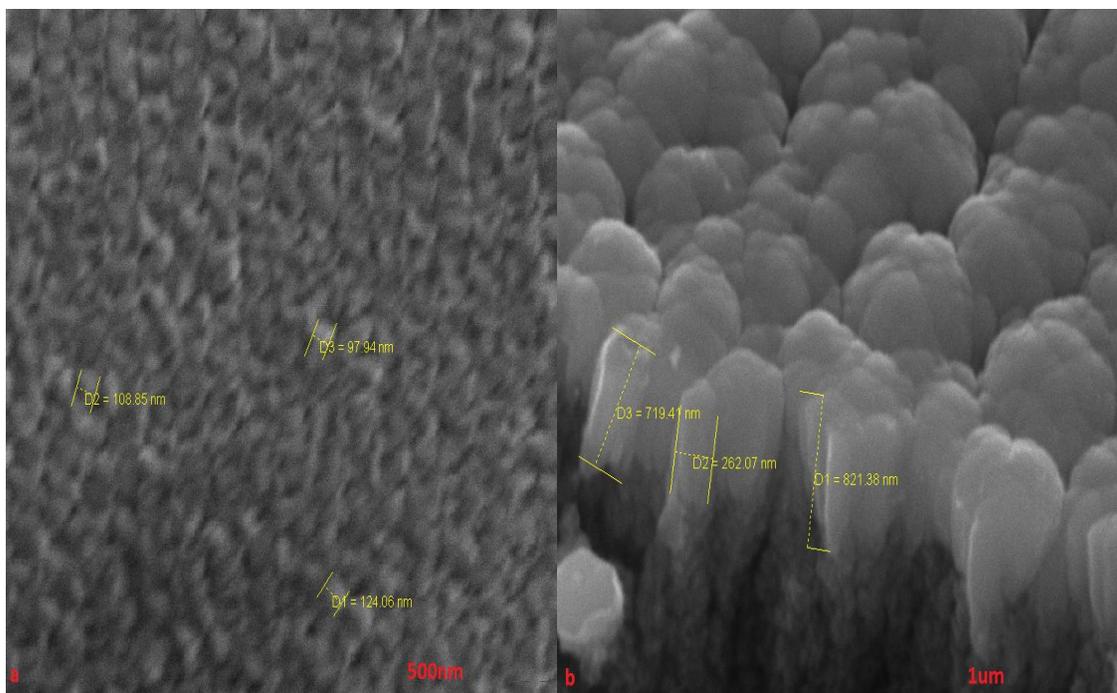


Figure 1: SEM image of as grown TiO_2 NRs ,grown at temperatures of a) 567°C , b) 650°C

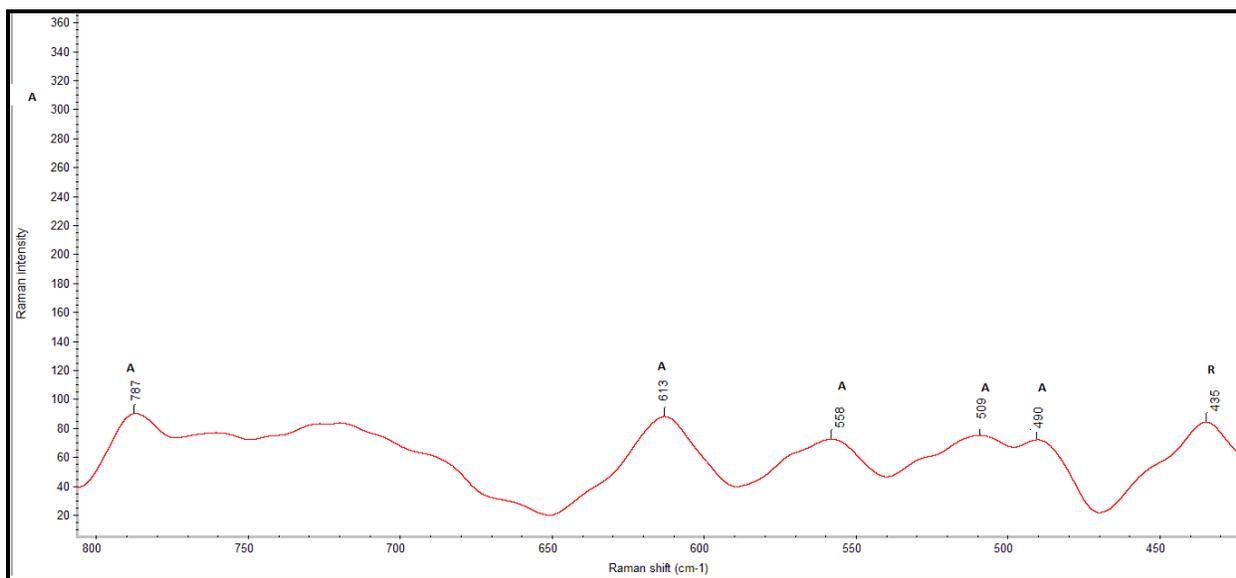


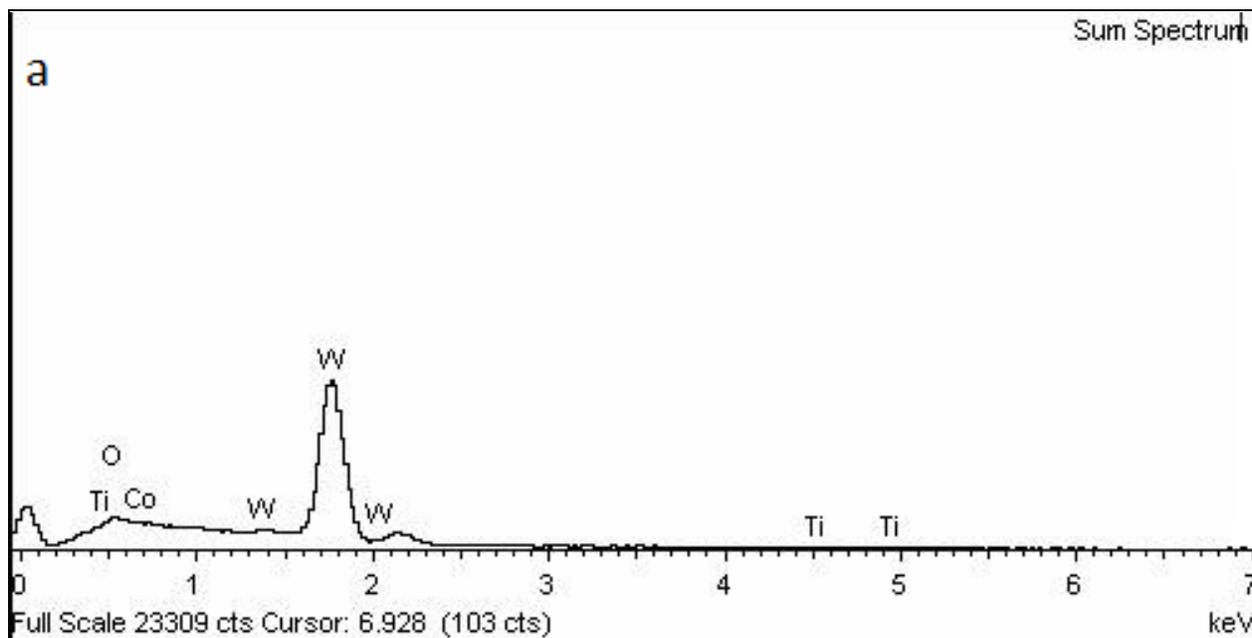
Figure 2: Raman spectra of the TiO_2 at 650°C

Fig 3a shows the results of EDX analysis at 15 min and 567°C . Here, signals are those of Co and O and Titanium(Ti). Weight percentages of Co and O are

0.5 and 17.38 respectively. Weight percentage of the Ti on Co catalyst is 0.2 %. Fig b shows signals related to the O, Co, Ti,C found in TiO_2 nanorods.

This is the situation at 30min and a temperature of 650 °C. Weight percentages of C, O and Co are 3.54 respectively. Weigh percentage of Ti under these conditions is 0.13 percent. Fig 4 shows the results of Dot mapping analysis at 567 °C, 650 °C. Fig a shows the sample surface at 15 min time and at a temperature of 567 °C. Red dots on the surface represent Ti, the resolution of the image being 20µm. Fig b shows the surface at 30min time and at a temperature of 650 °C. It can be seen that the amount of Ti increases with time and also with temperature. We can surmise from d that Ti has penetrated deep unto the nanorods. Fig 5 shows the results of XRD analysis. The analysis was done at 0.2 steps. 34.37,

, 14.9 and 0.05 percent 45.3,51.9,69.27 shows (110),(101),(111),(211) surfaces for the Rutile phase, 47.01,71.19 Shows (103),(211)Surfaces for the anatase phase, 56.6, 65.8 shows (111),(200) Co surfaces, 1.24 shows (331) Si surfaces, and 54.8,67.75,42.4,20.8,36.5 shows (202),(212),(200),(100),(331) surfaces for SiO₂.



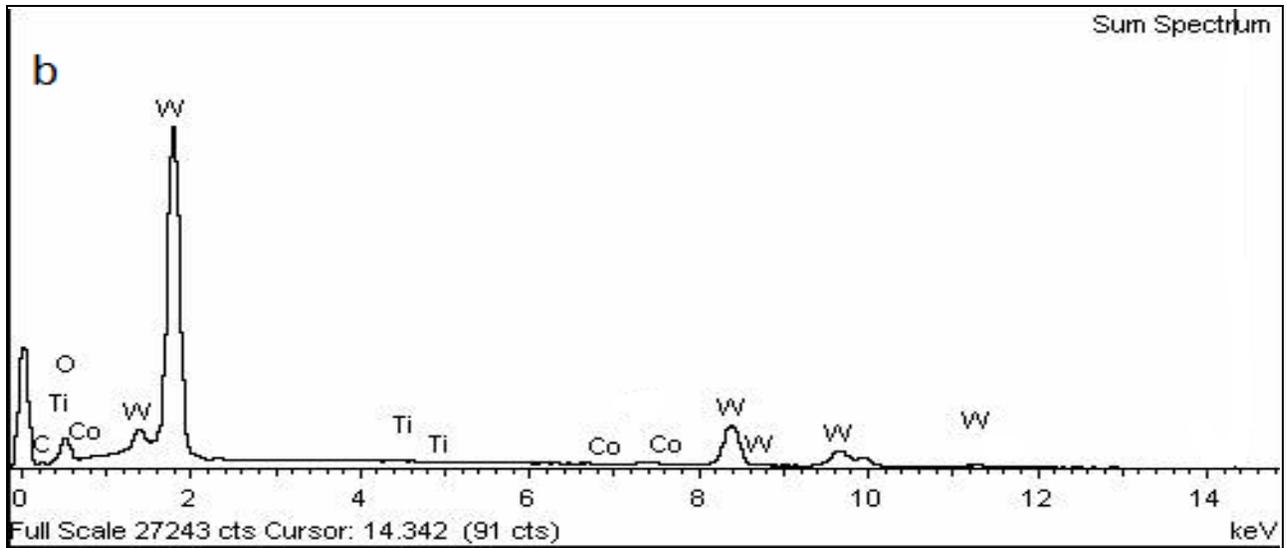


Figure 3: EDX Fig shows the surface and at a temperature of a) 567°C b) 650°C.

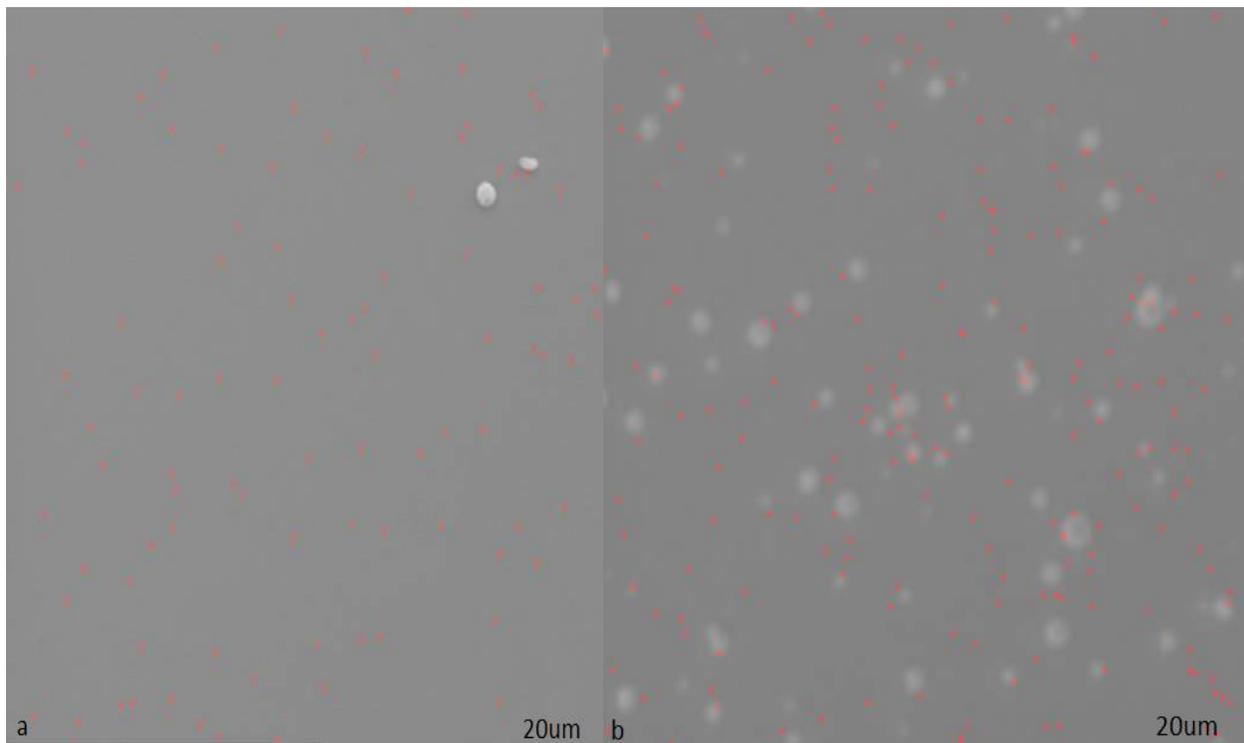


Figure 4: Dot mapping image shows the surface at 15min and 30min times and at a temperature of 567,650°C

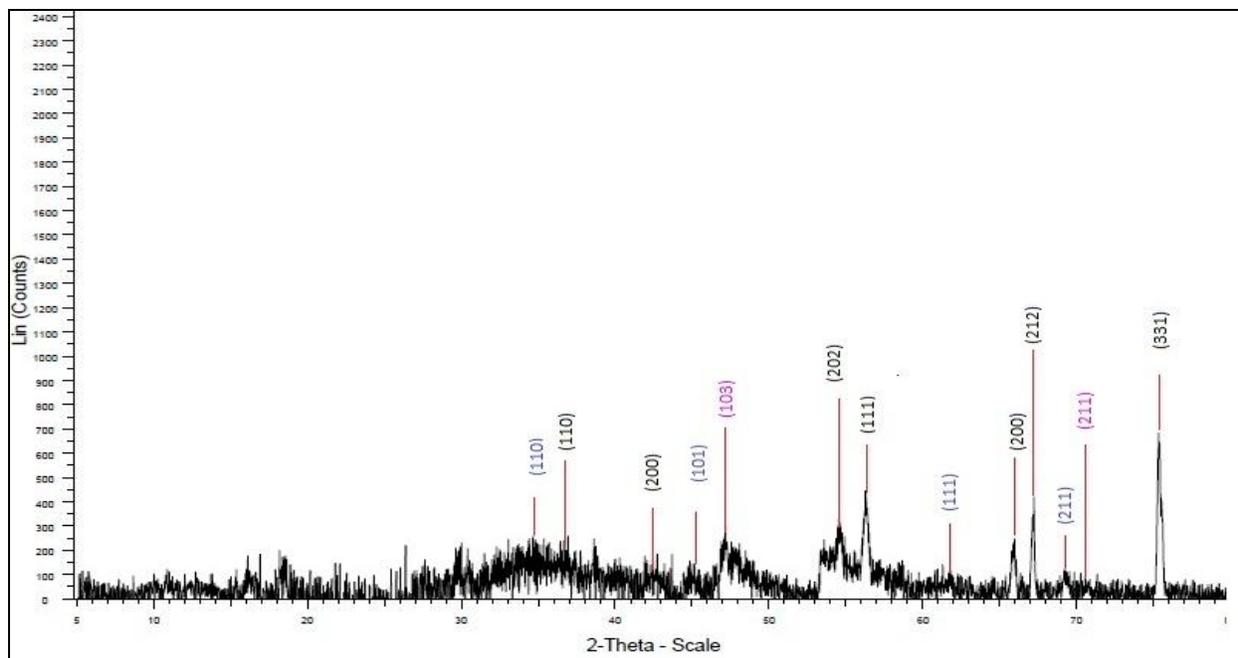


Figure 5: XRD of the TiO₂ Nanorods at 30 min and a temperature 650°C

4. Conclusion

Using Chemical Vapor Deposition method and the heated filament, we were able to manufacture TiO₂ nanorods. Considering the picture of SEM results, at a temperature of 650 these nanorods have diameter and length of 821.38 nm and 262.07nm respectively.

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The XRD analysis results showed that TiO₂ nanorods are crystallized either as anatase or as rutile. EDX analysis and dot mapping results showed that weight percentage and permeation of titanium unto the surfaces increases with time and with temperature. Also length and diameter of nanorods improve with time and temperature.

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6. References

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