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Synthesis of TiO^{1}_{2} Structure at Low Hydrothermal Temperature for Biosensor Application

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ABSTRACT

Synthesis of TiO_2 wires was prepared by using two steps method. TiO_2 seed layer was prepared using sol-gel method while TiO_2 wires were grown by using hydrothermal method. The annealing time and temperature during hydrothermal method were varied from 1, 4, and 5 hours and 110 and 120 °C respectively to analyze the effect towards the growth of TiO_2 wires. The morphology of TiO_2 wires formed was characterized using scanning electron microscope (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD). The electrical characterization of the TiO_2 wire based biosensor was conducted using electrochemical analysis. The cyclic voltammetry response was observed to analyze the performance of the glucose biosensor. The TiO_2 wires have shown a good response towards glucose detection.

Keywords: titanium dioxide, hydrothermal, electrochemistry, biosensor

1. INTRODUCTION

Recently, Titanium Oxide, TiO_2 nanostructures are being widely studied because of its distinctive optical, chemical and electrical properties [1]. TiO_2 is a multifunctional inorganic material that have non-toxic properties, chemically inert and thermally stable when added with other metals and semiconducting materials [2]. TiO_2 have a high sensitivity and specificity for fast analyte detection and great biocompatibility thus allowing this material to be selected as biomolecule identification in biological system [3]. Moreover, TiO_2 is also being used as surface protective layer of a diversity of metal because this metal oxide is stable, recyclable and insoluble in both acid and alkaline solution [4].

TiO_2 nanostructure such as nanotubes, nanorods, and nanowires are being used widely in various application such as in dye sensitized solar cell [5], lithium ion batteries, photocatalyst and biosensor [2].There are several methods to prepare TiO_2 nanostructure such as sol-gel method [4], chemical vapor deposition (CVD) [7], hydrothermal method [3,6,8] and sputtering technique. The hydrothermal synthesis is dependent on many factors such as growth temperature, time, and precursor concentration and so forth [6]. The wires can be formed leading to different morphologies by controlling these parameters. The morphology and structure differs among researchers.

As reported by Hwang et al. (2012), rutile TiO_2 wires with length ranged from 0.28 to 1.8 μm were grown on FTO substrate with hydrothermal growth temperature of 200 °C [8]. Besides,

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synthesis of TiO_2 wires made by Kumar et al. (2010) proved only individual wire obtained at 150 °C and tree-like structure of wires were obtained at hydrothermal growth temperature of 180 °C [9]. In another study made by Asiah et al. 2013, the hydrothermal synthesis of TiO_2 wires were temperature depended [6]. Based on the morphology of wires formed, the suitable hydrothermal growth temperature ranged from 100 to 180 °C [6]. These show that the hydrothermal growth temperature used by the previous study was quite high.

In this paper, synthesis of TiO_2 wires involves two steps method firstly sol-gel coating on the substrate and secondly hydrothermal synthesis which grew the wires. Hence, this paper is focusing on the fabrication of TiO_2 wires on a silicon oxide wafer substrate with a much lower hydrothermal growth temperature of 111 and 121 °C in an autoclave. The morphology of TiO_2 wires was analyzed and characterized by using Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD). TiO_2 wires formed on the substrate were used as a biosensor platform for the detection of glucose.

2. MATERIAL AND METHODS

Titanium Dioxide (TiO_2) solution was prepared by using Sol-Gel method by mixing ethanol (solvent), Titanium isopropoxide (precursor) and acetic acid (stabilizer) with a ratio of 9:1:1 by using magnetic stirrer for an hour [3]. The Sol-Gel solution was spin coated on the silicon oxide wafer substrate for 5 layers and further annealed at 550 ºC for 1 hour in a furnace [3].

TiO_2 wires were synthesized by using hydrothermal method. Firstly, hydrochloric acid (HCl) was added to Deionized (DI) water and stirred for 10 minutes [3]. Then, Titanium isopropoxide was added to the mixture and stirred continuously for another 10 minutes before poured it in a autoclavable bottle [3]. The substrate that had been annealed was placed into the mixture with the coated side facing down and further annealed in autoclave at 121 ºC and 111 ºC for 1,4 and 5 hour [3]. Then, the substrate was cleaned by using ethanol and DI water and left aside to dry. The morphology of synthesized nanowires was characterized by using JEOL JSM-6460LA scanning electron microscope (SEM). Figure 1 shows the process flow of TiO_2 wires synthesis

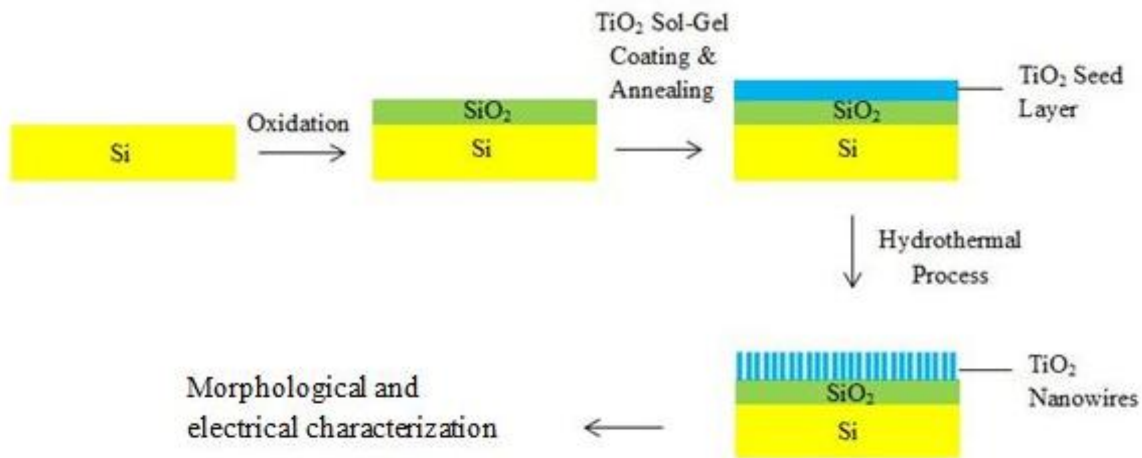
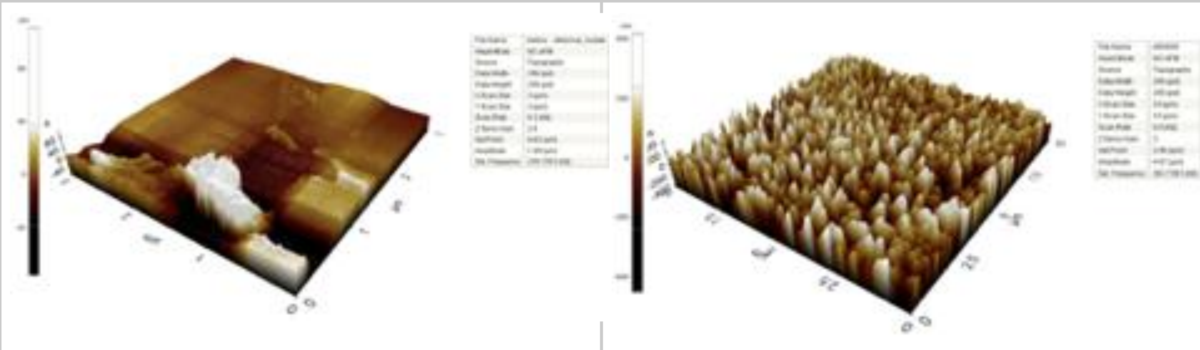


Figure 1. Process flow of TiO_2 wire synthesis

3. RESULTS AND DISCUSSION

3.1 Morphology of TiO_2 Thin Film

A thin layer of TiO_2 seed was formed by annealing the Si wafer substrates coated with TiO_2 sol-gel solution in a furnace for 1 hour at 550 °C. There was no wire formed during this process. The wires started to grow after going through hydrothermal process in autoclave. The coated side of substrate that was kept facing down during the hydrothermal process allows the crystal structure of TiO_2 to grow towards the direction of gravity thus forming the wire structure. The morphology of TiO_2 thin film was characterized using Atomic Force Microscopy (AFM). Figure 2 (a) and (b) shows the AFM images of substrate without and with the presence of wires respectively. The roughness, Ra value of sample without wire is 11.034 nm. Meanwhile, the roughness of sample with wires is 98.131 nm. The higher value of Ra indicates that the samples have higher roughness. Hence, the sample without the presence of wire is smoother compared to the sample with wires.

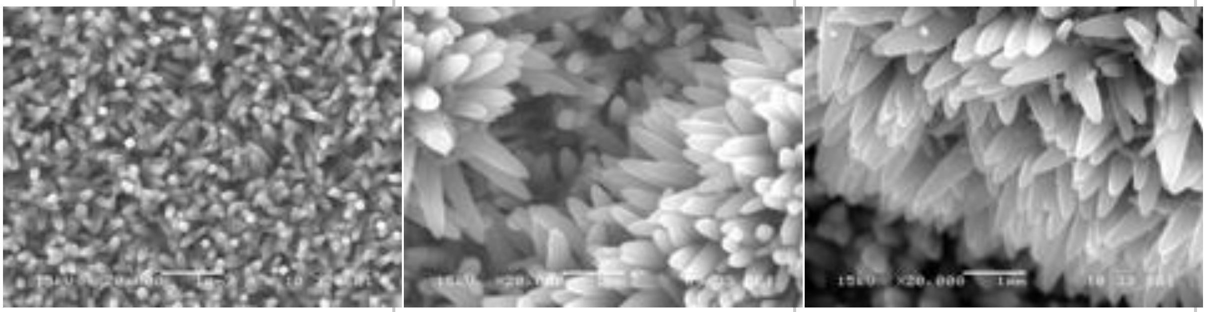


(a) (b)

Figure 2. AFM images of TiO_2 thin film. (a) Before hydrothermal process (b) After hydrothermal process

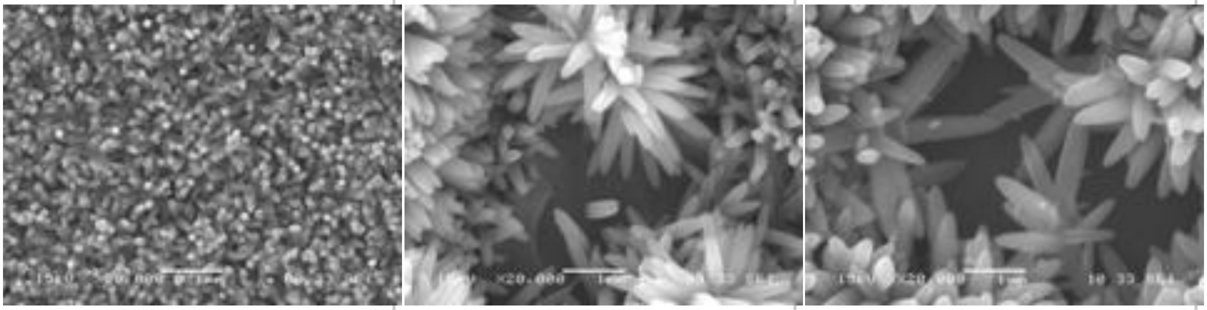
3.2 Effect of Annealing Time and Temperature towards the Growth of TiO_2 Wire

TiO_2 wires were formed by using the hydrothermal method in an autoclave at a temperature of 121 °C. The annealing time in the autoclave was varied for 1 hour, 4 hours and 5 hours to analyze the effect of annealing time towards the growth of wires. The growth of TiO_2 wires was characterized using JEOL JSM-6460LA scanning electron microscope (SEM). Figure 3 shows the



(a) (b) (c)

SEM images (×20000) of TiO_2 wires annealed for 1, 4 and 5 hours at 121 °C. Based on the observation, the wires are completely formed by 1 hour annealing time and there is no significant difference between wires annealed for 1 hour, 4 hours and 5 hours. The average length of wires grown at this temperature for 1 hour, 4 hours and 5 hours annealing are 852 nm, 1389 nm, and 1126 nm respectively. While the average diameter of the wires for 1 hour, 4 hours and 5 hours annealing are 171 nm, 278 nm, and 235 nm respectively. The average length and diameter was obtained by considering 10 values of length and 10 values of diameter for each sample.



(a) (b) (c)

Figure 3. SEM images of TiO_2 wires annealed at 121 °C for (a) 1 hour (b) 4 hours and (c) 5 hours

Since the annealing time does not give a significant effect to the morphology of the wires, the hydrothermal temperature was decreased to 111 °C to determine whether the change in temperature affect the growth of wires. Figure 4 shows the SEM images (×20000) of TiO_2 wires annealed for 1, 4 and 5 hours at 121 °C. Based on the observation, the temperature also does not affect the growth of wires. The average length of wires grown at this temperature for 1 hour, 4 hours and 5 hours annealing are 774 nm, 436 nm, and 2948 nm respectively. While the average diameter of the wires for 1 hour, 4 hours and 5 hours annealing are 115 nm, 262 nm, and 297 nm respectively.

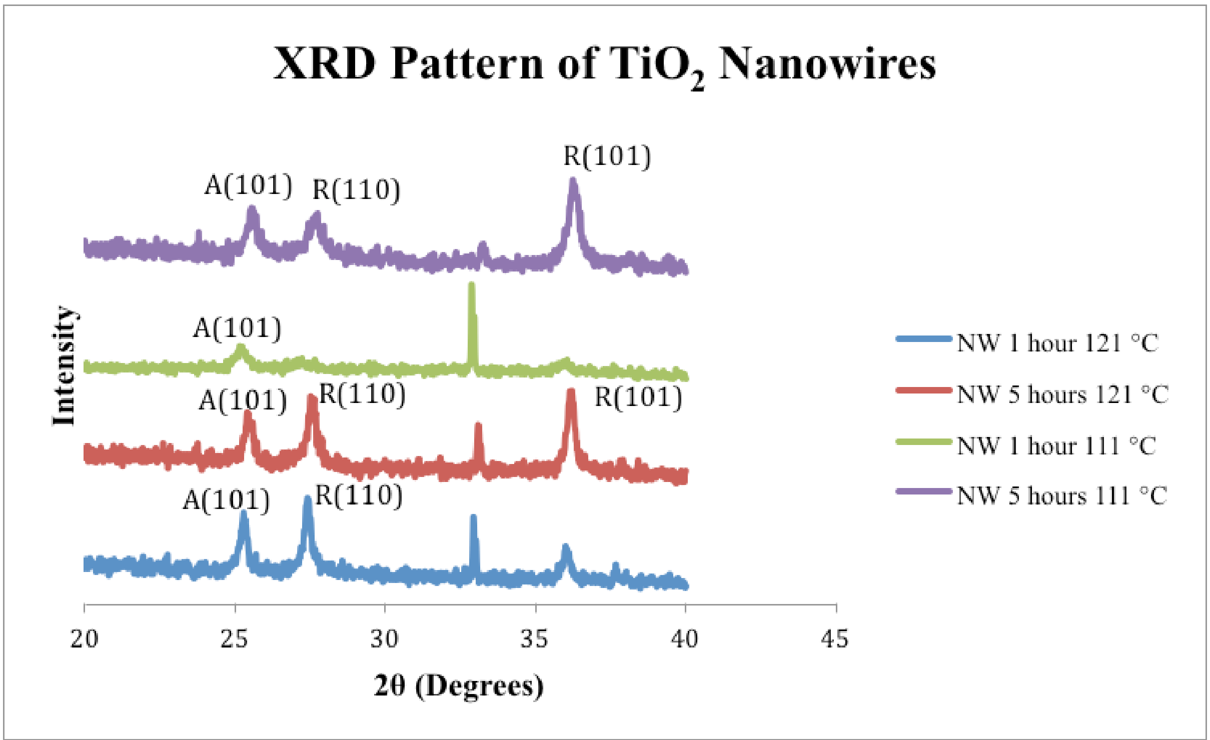
Figure 4. SEM images of TiO_2 wires annealed at 111 °C for (a) 1 hour (b) 4 hours and (c) 5 hours

The wires obtained were in micro scale. The growth trend of wires by varying the time and temperature of hydrothermal process fluctuates. Hence, the annealing time and temperature are not the strong factors that affect the growth of wires. It is assumed that the positioning of silicon substrate with TiO_2 seed layer during hydrothermal process limited the growth of wires.

3.3 Characterization of Crystal Structure of TiO_2 Wires

The crystal structure of TiO_2 wires was studied using X-Ray Diffraction (XRD). The XRD characterization was conducted for the substrates that had been annealed in autoclave for 1 hour and 5 hours at 121 °C and 111 °C. Figure 5 displays the XRD pattern of these substrates from 20° to 40°. The figure describes there is a significant difference between each annealing time and temperature by observing at the phase and intensity of the wire structure.

The XRD pattern of wires annealed for 1 hour at 121°C clearly displays distinct peaks at 25.26° and 27.37° corresponding to anatase (101) and rutile (110) reflection respectively. Meanwhile,



the wires annealed for 5 hours at the same temperature shows 3 distinct peaks at 25.39°, 27.52° and 36.14° correspond to anatase (101), rutile (110) and rutile (101) respectively.

Next, the XRD pattern of wires annealed for an hour at 111 °C shows only one reflection peak that match with TiO_2 crystal structure. The peak is at 25.09° which correspond to anatase (101). Meanwhile, XRD pattern for substrate annealed for 5 hours at the same temperature shows 3 peaks obtained at 25.15°, 27.45° and 36.24° which correspond to anatase (101), rutile (110), and rutile (101) respectively. Therefore, the diffraction peaks can be indexed as rutile and anatase mixed phase. Thorough observation at peak 32.5°, the silicon substrate peak was revealed which correspond to Si(200) [10]. At this reflection peak, the intensity is lower for longer annealing time at both temperature. It indicates that the silicon substrate was fully covered with TiO_2 wires on the surface hence lower Si intensity peak. It shows that 5 hours annealing time allows better distribution of TiO_2 wires growth on the substrate compared to only 1 hour annealing time during hydrothermal process.

Figure 5. XRD pattern of TiO_2 wires from 20° to 40°

3.4 Electrochemical Analysis of TiO_2 Wires for Glucose Detection

The electrochemical analysis of TiO_2 wires using Autolab Potentiostat results in the linear sweep cyclic voltammetry response as shown in Figure 6 at from 0 V to 1 V in PBS (0.01M, NaCl, KCl, pH 7.4) at room temperature as a controlled condition. The analysis was executed at a scan rate of 0.1 Vs^{-1}. The analysis was conducted using substrate with TiO_2 wires that was annealed in autoclave for 1 hour at 111 °C. Based on the cyclic voltammetry response, there is no oxidation and reduction peaks were observed because the rate of electron transfer between the wires is very fast.

As for the conductivity of the wires, the value of current is the lowest when no glucose added. Then, the current increased when glucose was added to the PBS solution. When 1 V of potential is applied, the value of current is approximately 30 µA. By replacing the PBS with Potassium Ferricyanide, $K_3[Fe(CN)_6]$ (5 mM) the current is highest. At 1 V potential, the value of current is approximately 0.16 mA. $K_3[Fe(CN)_6]$ has conducting properties hence giving higher value of current compared to PBS. Therefore, the analyte (glucose) can be detected using TiO_2 wires.

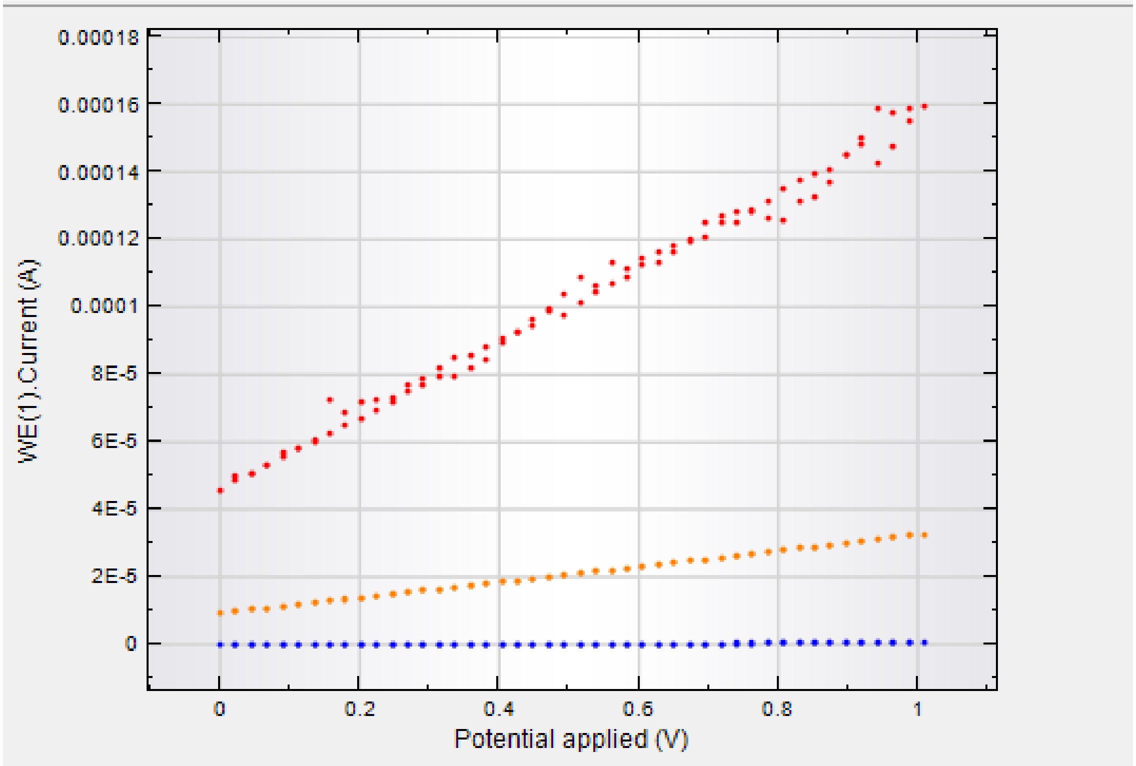


Figure 6. Cyclic voltammogram response of TiO_2 wires in 0.01M PBS, 0.01M PBS + 0.25 M glucose and 5mM $K_3[Fe(CN)_6]$ + 0.25 M glucose

4. CONCLUSION

The wires were successfully grown on the substrate based on the morphological characterization made by SEM and AFM by using low hydrothermal growth temperature of 111 and 121 °C by a minimum of one hour annealing. From the XRD analysis, different annealing time and temperature give different phase and intensity of the structure. The TiO_2 wires have shown a good preliminary response in detecting glucose based on the electrochemical analysis.

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