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Research Paper

Fabrication of TiO_2 thin film using anodization of Ti and its application for gas sensor

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Abstract
Metal oxides semiconductors such as TiO_2, ZnO and NiO etc. are widely available and nontoxic, have chemically stability, large band gap, remarkable structural, photochemical, electronic, and optical properties. These materials gained more attention in the field of sensors, and consumer electronics. Here we report the synthesis of TiO_2 nanotubes using anodization of Ti. The structure, optical properties, and morphological composition of synthesized TiO_2 nanotubes, are reported. The TiO_2 was grown on Ti by anodizing in electrolyte solution containing 0.5 grams of ammonium fluoride, 2 vol% ethylene glycol, and 98 vol% in DI water, at potential difference of 40 V. The fabricated samples were characterized using SEM, AFM and XRD. Surface morphology was studied using scanning electron microscopy. Morphological and structural investigations revealed that the as-grown TiO_2 nanotubes were in closed packed hexagonal structure which was perpendicular to the Ti surface. The presence of rutile and anatase phases in the sample is evident from XRD results. To validate the SEM findings, the sample was characterized with 3D AFM. An H_2 gas sensor was fabricated using the synthesized nanoporous film. The sensor shows a decrease in resistance and increase in current when it is exposed to H_2.
Key words: *Anodization, TiO_2, Nanotubes, Nanoporous film, Gas sensor*

I. Introduction

Metal oxides semiconductors such as SnO_2, ZnO, WO_3 and TiO_2 etc. are widely used for photovoltaic sensors and memory application and they have chemically stable properties because of its large band gap, widely available and nontoxic [1]. The crystalline TiO_2 metal oxides are one of the most used materials in environment cleaning application and photocatalyst because of remarkable structural, photochemical, electronic, and optical properties it gains more attention in the research field [2]. The TiO_2 films changed accordingly the conversion of metals into their oxides as a result of heating to a high temperature from amorphous to anatase and rutile [3].

To achieve TiO_2 nanoparticles much research was performed in the previous few years such as sol-gel approach [4], the solvo-thermal method [5], the hydrothermal method [6], and anodization method [7-8] etc. Although the chemical approach to the synthesis of TiO_2 NPs is popular because it is simple and allows for control over the size and form of the NPs, it has drawbacks, including high energy costs, high temperature and pressure, ecotoxicity, and environmental sustainability and additionally, this restricts their ability to be produced in large quantities and their potential uses in a variety of disciplines [9]. Titanium dioxide films can be deposited onto the substrate by using some simple and cost-effective methods such as electrochemical deposition [10], hydrothermal method [11], spray pyrolysis [12], sputtering [13], chemical bath deposition method [14], screen printing method [15], pulse laser deposition [16], and spin coating method [17] etc. Nowadays electrochemical deposition techniques for manufacturing of TiO_2 nanoparticles and films were often used because it is very simple, low cost and the size of various nanostructures can be easily controlling such as well aligned nanotubes without taking help of any expensive equipment and these nanostructures the photocatalytic properties of TiO_2 nanoparticles increases because surface area is enhanced [18].

Firstly, titanium dioxide is used for water splitting application which was given by Fujishima and Hondain 1972 but now it is also used for environmental application and many other applications gas sensors etc [19]. The researcher used crystalline TiO_2 for environmental clean-up, gas sensors [20-22] hydrophilic coating, photovoltaic applications [23], electrocatalysis for energy [24], photo electrochemical and many other applications by using the 1D and 3D titanium dioxide nanorods, nanowires, nanoflakes [25]. Titanium dioxide is a significant metal oxide semiconductor (MOS) that is utilized in a variety of electrical applications, the most common of which being gas sensor applications, because of this the sensing applications of anatase and rutile TiO_2 were thoroughly investigated, and descriptions of surface processes employing oxidizing or depleting gases were introduced; this in turn changes the conductivity of the film [26]. TiO_2 is an n-type semiconductor, and there are two fundamental kinds of metal oxide-based semi-conductive sensors: n-type, which has a majority of electrons, and p-type, which has a majority of holes [27]. Typically, reducing gases such as NH_3, CO, H_2, HCHO, and others cause n-type semiconductors' conductivity to increase and p-type semiconductors' conductivity to decrease, whilst NO_2, O_3, Cl_2, etc. oxidizing gases have the opposite effect [28].

In this research TiO_2 is synthesized by anodization of titanium, and then it is used to fabricate gas sensor. The structure, optical characteristics, and morphological makeup of TiO_2 nanotubes, which were produced by anodizing them in a solution including 98 vol% of DI water, 2 vol% of ethylene glycol and 0.5 gram of ammonium fluoride, were examined in this investigation. The as-grown TiO_2 nanotubes were found to be crystalline making anatase and rutile structure. By using TiO_2 onto titanium a gas sensor is fabricated and examined for detection of H_2 gas.

II. Materials and method

Material: 99.99 % pure Titanium sheet was purchased from Goodfellow, analytical grade acetone, 2 propanol, ethylene glycol, ammonium fluoride, and nitric acid were purchased from Sigma Aldrich. The Au sputtering and DI water was used locally from department of Physics University of Balochistan, Quetta.

Fabrication Method

The methodology for the synthesis of TiO_2 nanotubes and fabrication of gas sensor can be divided in two steps. The first step involves anodization of Ti for synthesis of TiO_2 nanotubes. The second step consists the method to fabricate the gas sensor using TiO2 nanotubes. The details of these steps are given below along with details of the materials, equipment and devices used in the process. Ti sheet was cut into 2 cm x 2 cm square pieces. The samples were cleaned in acetone and 2-propanol for 10 minutes in an ultrasonic bath and then rinsed DI water to remove chemicals from surface. The chemical polishing was performed in 6 M HNO_3 for 10 minutes and rinsed in DI water. Three steps of anodization were used first step for 2 h, second step for 12 h, and third step for 3 h in 98 vol% of DI water, 2 vol% of ethylene glycol and 0.5 gram of ammonium fluoride at a potential difference of 40 V and at a constant temperature of $0^{O}C$. The anodization was performed in two electrode setup as shown in Figure 1.

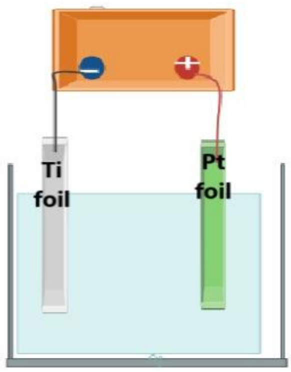


Fig.1. Schematic of anodization setup

After anodization the samples were annealed at $500^{0}C$ for 2 h to obtained the crystalline structure of TiO_2. The gas sensor was fabricated sputtering Au patterned electrode on TiO2 surface as depicted in Figure 2.

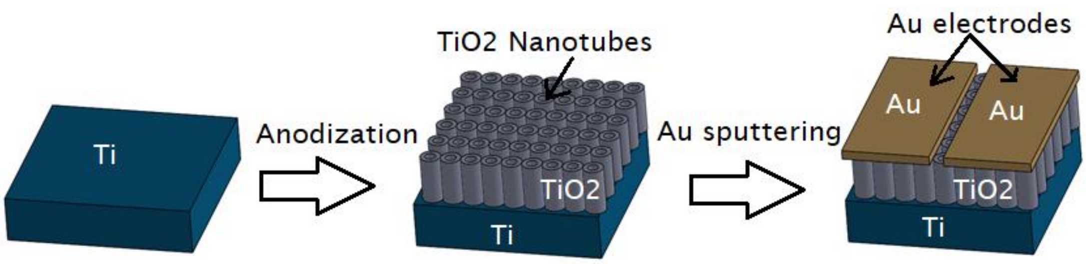


Figure 2: Schematic of fabrication process for H_2 gas sensor

III. RESULTS AND DISCUSSION

Anodization of Ti substrate in three steps produced TiO_2 nanotubes closely packed making a nanoporous membrane structure. Figure 3 shows the SEM images TiO_2 surface, barrier side and cross-section. Figure 3 (a) depicts regular arrangement of TiO_2 nanotubes packed in hexagonal form where the pore diameter is from 40 nm to 130 nm. The boundary of each tube is very clear. The variation in pore and tube diameter is due to up and down in Ti surface which produces variation in electric field during anodization. Due to variation of electric field on Ti surface different diameter of nanotubes are formed. For analyzing the back side the TiO_2 membrane was peel off from Ti surface using sticking tape. Figure 3 (b) shows the back side of TiO_2 which consist of barrier layer closing all the tubes at the bottom and making hexagonal arrangement of cells. The variation in tube/cell diameter is also found at barrier side. Figure 3 (c) shows the cross-sectional image of TiO_2 where all the tubes are arranged parallel to each other.

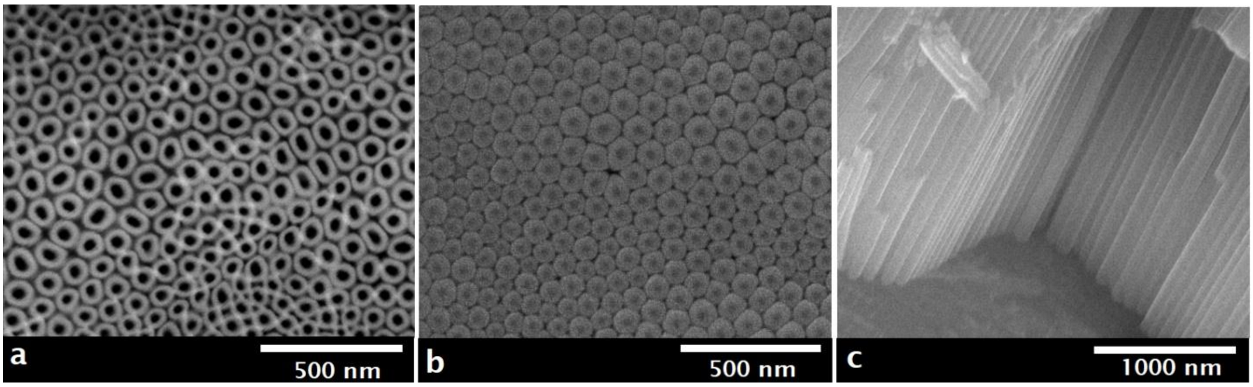
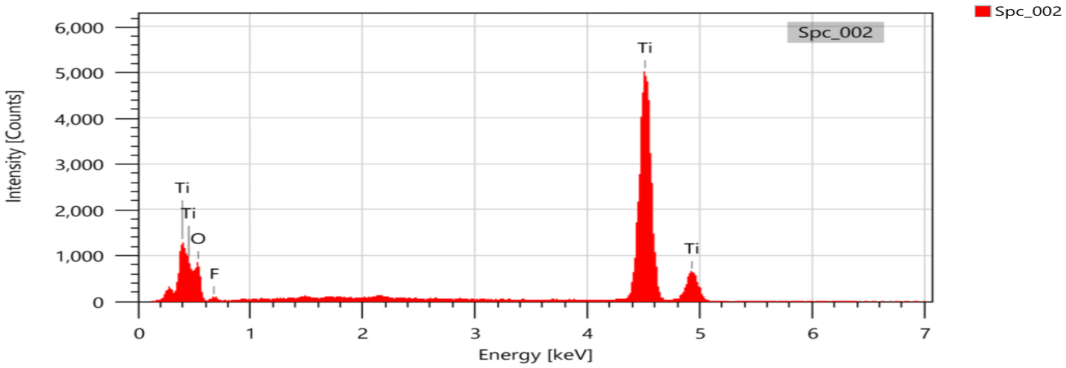


Fig. 3. SEM image of the synthesized titanium nano porous membrane from the bottom side with the barrier layer following the third anodizing stage and (b) SEM image of TiO_2 after the barrier layer was removed (c) cross sectional area of TiO_2

The chemical composition and elemental analysis of the surface of the nano porous barrier-free titania membrane that was produced following three anodizing step were investigated using energy-dispersive X-ray (EDX) spectroscopy. Figure 4 displays the analysis's findings of chemical composition of prepared pattern. In accordance with the EDX data, shows that titanium and oxygen are present in the nano porous titania membrane as soon as it is formed. As a result of this element's adsorption in the barrier layer from the anodization solution, fluorine traces were also detected.



Name	O	F	TiO2	Total
Spc_002		2.47	97.53	100.00
Average		2.47	97.53	
Standard Deviation				

Mass%

Fig.4. The nanostructure's EDX analysis results from the barrier layer side following the third anodizing stage.

Figure 5 shows an X-ray diffraction pattern of fabricated TiO_2 on Ti substrate which was further annealed at 500 °C. The presence of rutile and anatase phases in the sample is evident at several points as indicated by circle and triangle. The larger peaks as labeled with square indicated the presence of Ti. The observed peaks at 24.89°, 38.03°, 62.6° and 75.9° indicates the presence of anatase TiO_2, the peaks at 34.7°, 39.79°, 52.64°, 70.33°, indicates the presence of titanium and the peaks at 29.08° indicates the presence of rutile TiO_2. These peaks are due to Ti substrate on which the TiO_2 is fabricated.

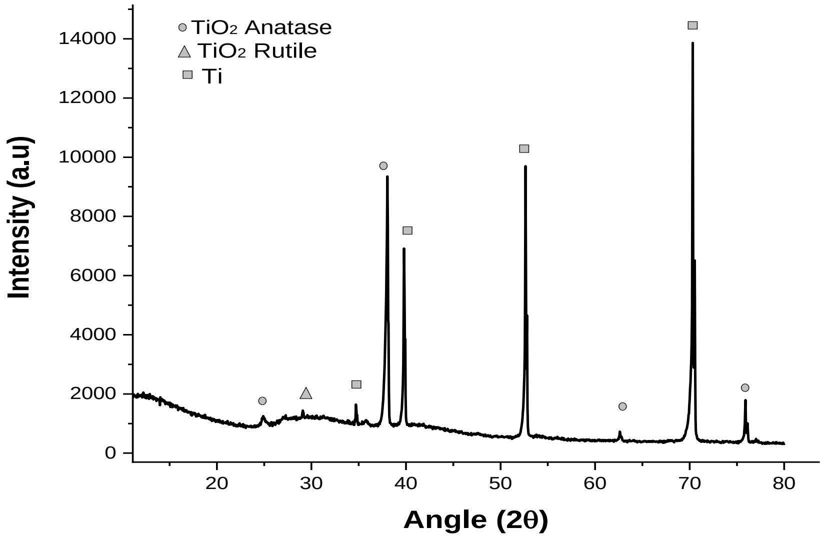


Fig.5. XRD results of TiO_2 using three step of anodization

To validate the SEM findings, the sample was characterized with 3D AFM. The AFM is taken for the depth of 100nm where reading from blue to pink color shows the depth and height of features as shown in figure 6. From this result it is very clear that the grown TiO_2 structure is porous and each cell (tube) has six spikes on it top where cells are attached with each other.

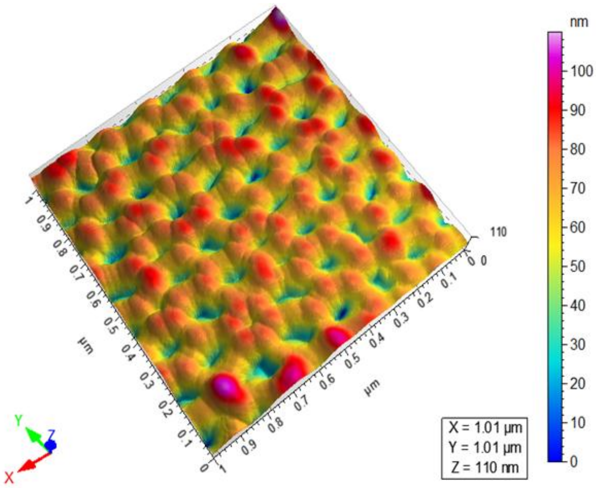


Fig.6. AFM results of nanoporous TiO_2

TiO2 Gas sensor

The TiO2 gas sensor was fabricated according to the processing steps as explain in Figure 2. The Au patterned electrodes were sputtered on TiO2 surface using DC plasma sputter with Argon atmosphere at vacuum level of 10^{-2} Torr. The thickness of Au layer was around 20nm. Both of the Au segment was then connected with Cu wire using Silver past. Where the TiO_2 layer act as channel, and the two electrodes as source and drain. The fabricated sensor was then exposed to H_2 and source to drain current was measured at applied voltage of 5V. The sensor was exposed to different concentration of H_2 and the source to drain current was recorded in each case as shown in Figure 7. From the graph it is clear that with out exposure of H_2 the current is very low where sensor is considered as OFF and when it is exposed to H_2 the current increases. The peak value of current is dependent of concentration of H_2 the greater the concentration the greater is the current. At concentration of 250 ppm the peak value of current is 18 mA, current at 150 ppm is 8.4 mA, at 130 ppm it is 8 mA while at 50 ppm current is 3.5mA.

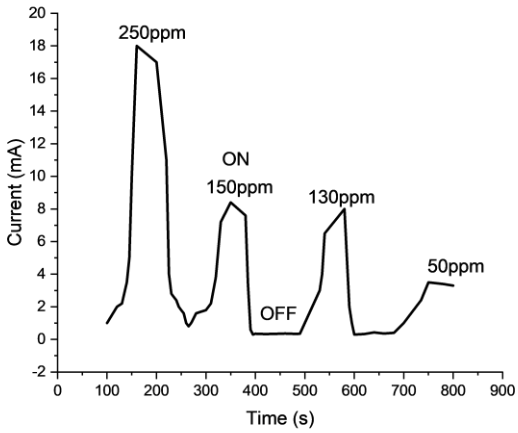


Figure 7: Plot between time and current at different concentration of H_2

IV. Conclusion

In this research TiO_2 was fabricated on Ti sheet using anodization. This study examined the morphological composition, elemental composition, crystallographic characteristics, and structure of TiO_2 nanoporous layer. The TiO_2 was characterized with the help of XRD, EDX, FESEM, and AFM. It was observed that through anodization the Ti surface converts into nanoporous layer which consist of TiO_2 nanotubes connected with each other. The XRD revealed that Rutile and Anatase states are present in the fabricated TiO_2 which was annealed at $500^{O}C$. TiO_2 is n-type material and its band gap is in visible region. The TiO_2 is sensitive to the H_2 which decreases its sheet resistance. Based on this property the TiO_2 gas sensor was fabricated to detect H_2. The fabricated sensor gave promising results for detecting various concentration of H_2.

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