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Preparation and characterization of titanium oxide nanoparticles using sol-gel method

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ABSTRACT

The titanium dioxide powder was prepared on p-type porous silicon by sol-gel process. The morphology of TiO_2 sensing film surface was imaged by atomic force microscope (AFM) model AA3000 SPM from Angstrom Advanced Inc. The average roughness of the film surface is 25 nm. The X-ray diffraction (XRD) patterns shows of TiO_2nano-particalprepared by the solgel method arepolycrystalline, the anatase phase with the preferential orientation of the crystallites along the [101] direction,at2θ =25.253°theresultisinagreementwiththe ASTM Card (PDF 21-1272).The resistance of the TiO_2nano-partical sensors reduces with the presence of vapor ethanol.

1. Introduction

Titanium dioxide (TiO_2) is an important inorganic functional material with good physical properties, which make it suitable for thin film applications. TiO_2 films have often been used in microelectronic devices [1,2]. TiO_2 thin films are also often used as various optical coating for its good transmittance in the visible region, high refractive index and chemical stability [3-5]. Recently TiO_2 has been widely investigated [6] because of its high efficiency of hydrogen generation and also its high photostability in an aqueous solution, which opens prospects for the use of TiO_2 thin films as photocatalyst, bactericide, photoanode, and gas sensor,etc.Gas sensors based on semiconductor metal oxide thin films focused numerous research efforts during the last few years [7]. The sensors based on these materials change their conductivity in the presence of oxidizing and reducing gases as electron density at the surface gets modified due t absorption and desorption of O^{-2}, O_2^- or O^-. This adsorbed oxygen gets trapped at the grain boundary trap states thereby increasing the grain boundary potential barrier. This culminated in an increase in resistivity of the material. For reducing gases, the trap get depleted of charged carriers and thereby reduce the resistance over and done with lowering of the potential barrier at the grain boundaries [8].It is well known that TiO_2 exists in three crystalline structures: rutile, anataseand brookite [9]. The anatase phase is especially adequate for those applications due to its crystal structure and a higher band gap of 3.2 ev compared to the 3 ev in rutile. Anatase and rutile have properties of interest for sensing applications. There are many methods to prepare TiO_2 films: chemical vapor deposition (CVD), thermal or oxidation of Titanium, electron beam evaporation, ion sputtering and the sol-gel method [10-12].The sol-gel technique has been used for making optical coatings about 50 years ago and in the last decade attracted more attention due to the intensive development of sol-gel process has certain advantages: Low process cost, low temperature of heat treatment, high evenness of the films and wide possibility to vary film properties by changing the composition of the solution, etc.In the present work, TiO_2 nanoparticles were synthesized by Sol-gel method and tried to study optical properties and structural properties. X-ray diffraction (XRD) and scanning electron micrograph (SEM) images are shown to clearly see the grain size.

2. Experimental Work

The titanium dioxide powder was prepared on p-type porous silicon by sol-gel process using titanium isopropoxide, $[Ti(OC_3H_7)_4]$, as a precursor and ethanol as a solvent. After dissolution of11.2 mL of $Ti(OC_3H_7)_4$ in ethanol, a solution of 0.73 ml water in ethanol was mixed and1 mL diethenol amine $[C_4H_{11}NO_2]$ addeddropwise under continuous stirring for 2h to realize a transparent sol. $Ti(OC_3H_7)_4$: C_2H_5OH: H_2O: $C_4H_{11}NO_2$ molar ratio was set at 4:140:4:1. The sol was digested for 24h and dried subsequently at 100oC for 10h, calcined for 2h elevated temperatures, and cooled at a rate of ~ 8.3 ^oC/min. Thermogravimetric analysis (TGA) of the dried sol-gel product was carried out by raising its temperature at a rate of 4^oC/min from 50 to 850^oC in air to ascertain the conditions of TiO_2 formation. Square-shaped p-types of single crystal silicon substrates, each of (1x1) cm^2 area, of (0.5-3) Ω.cm resistivity and (100) orientation. The Si samples were cleaned by alcohol with ultrasonic bath in order to remove the impurities and residuals from their surface. These substrates are etched with HF for 1 min to remove the native oxide. Thin homogenous PSi layer of various thickness were formed on the frontal surface of the material using two methods electrochemical (EC). The electrochemical cell is the important part of the fabrication system as the homogeneity of PSi samples depends on its structure. The electrochemical etching cell, used in this work, is schematically shown in Figure (1).

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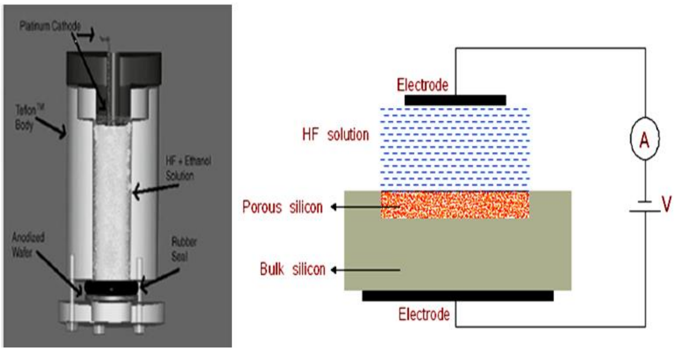


Figure 1. Electrochemical etching cell

3. Results and Discussions

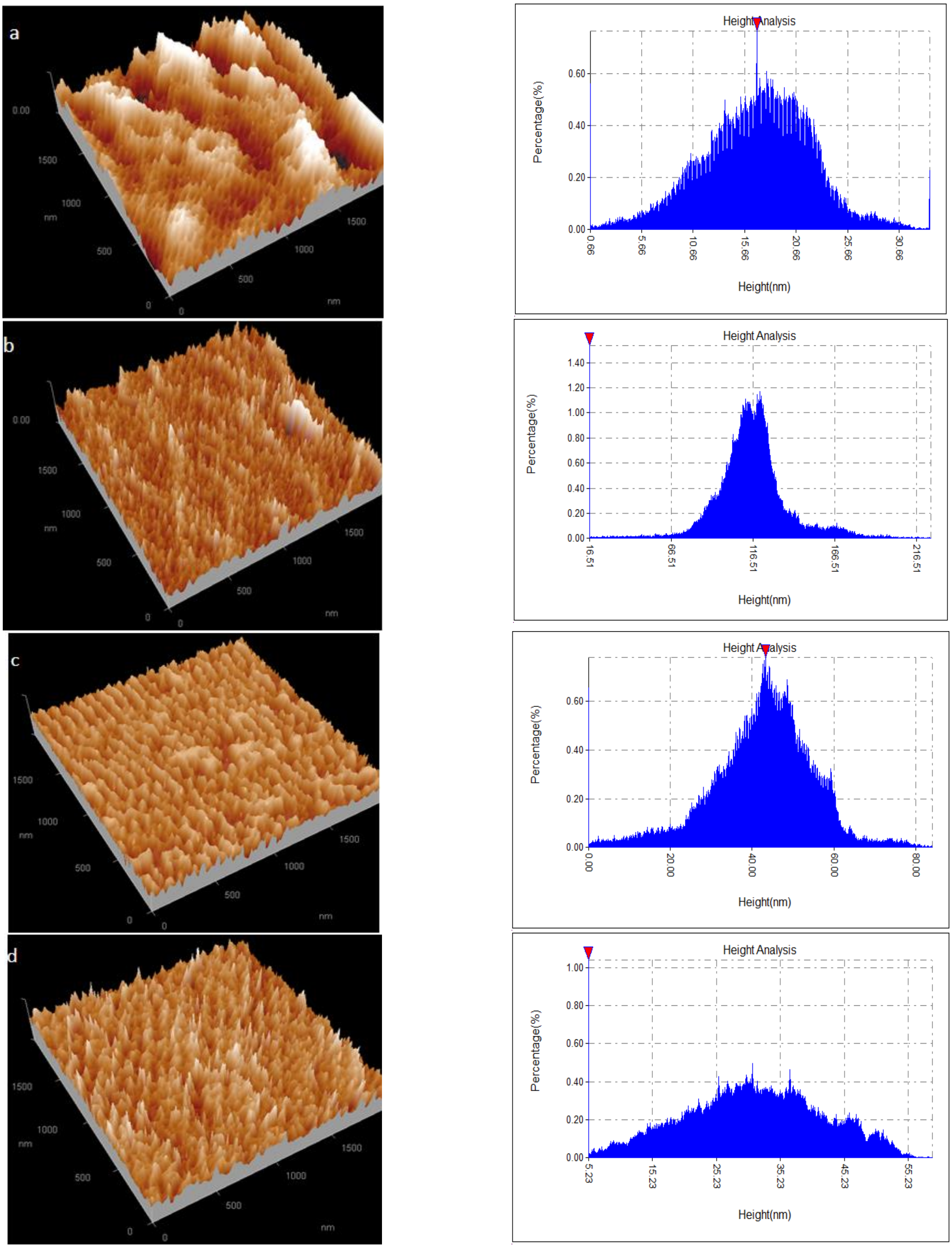


Figure 2. Atomic force microscope for TiO_2 nanoparticles at different annealing temperature

The morphology of TiO_2 sensing film surface was imaged by atomic force microscope (AFM) model AA3000 SPM from Angstrom Advanced Inc. Figure (2) shows the formation of TiO_2 nanostructure at different annealing temperature (400, 500, 600 and 700). AFM micrograph proves that the grains are uniformly distributed within the scanning area (2000×2000nm) with individual columnar grains extending upwards. The surface morphology of TiO_2 film obtained from the AFM analysis is shown in Figure (2). It obvious that surface is very smooth. The average roughness of the film surface is 25 nm. It is known that the surface properties of the transparent conducting oxide films influence their optical and electrical properties which are important factors for applications in optoelectronic devices; in principle, the increase in surface roughness of the films leads to a decrease in the efficiency for photovoltaic properties, and therefore, it is very important to investigate the surface morphology of the films. (Van and Dinh 1998). The AFM technique uses alaterally moving tip, while the cantilever reflects the sample's topography, or the Z measurements. Even though the tip is very sharp, it is impossible to gather the information from the underside of specimen. The spherical particle will be viewed as a bump by the AFM. To correct the AFM image for this effect, some deconvolution techniques are used. The grain size decreases with the increase in annealing temperature, while the films presented uniformity. Since the size grain decreases in dimension when the film thickness decreases, it suggests that the charge transport is occurring predominantly intragrain in cases of lower thickness, or equivalent to greater grains, and that there is a preferential charge transport inter-grain in greater thickness samples, where there are more interface grains; in this kind of microstructure, it is usually not dominated by bulk properties but by grain walls, which either act as low conductivity blockades or as high conductivity carrier accumulation regions. This surface characteristic is important for applications such as solar cells, gas sensors and catalysts (Gyogy and Axente 2000; Al-Hardan and Abdulllah 2009.

TiO_2 layers were studied by X-ray diffraction (XRD) techniques. It is a noncontact and nondestructive technique used to identify the crystalline phases present in materials and to measure the structural properties of these phases. In XRD was carried out done according to the ASTM (American Society of Testing Materials) cards taken from Match Program version 1.9b (2011). We used the measured (X-Ray) to determine the crystal structure that appears to us so that we can determine the knowledge and its applications, as they prefer the Rutile in photovoltaic applications for its ability to reflect light as it is more stable than Anatase. Either Anatase is preferred in the applications of optical catalysts because it has the ability to transfer a higher mobility of electric charges. Figure (2), shows the X-ray diffraction (XRD) patterns of TiO_2nano-particalprepared by the solgel method arepolycrystalline, the anatase phase with the preferential orientation of the crystallites along the [101] direction,at2θ =25.253°theresultisinagreementwiththe ASTM Card (PDF 21-1272).

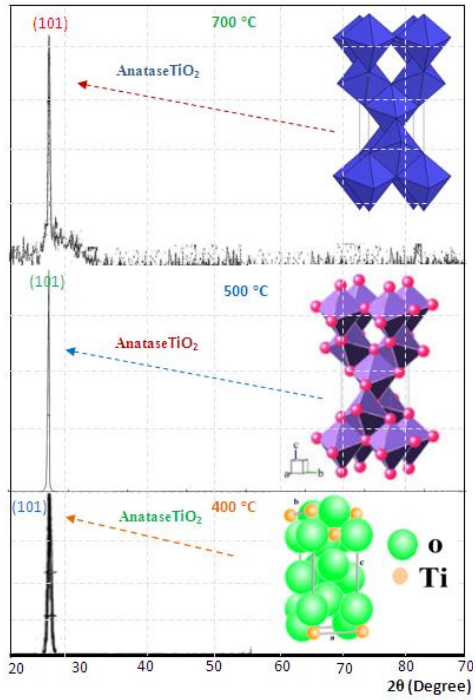


Figure 3. XRD patterns for TiO_2 nanoparticles at different annealing temperature.

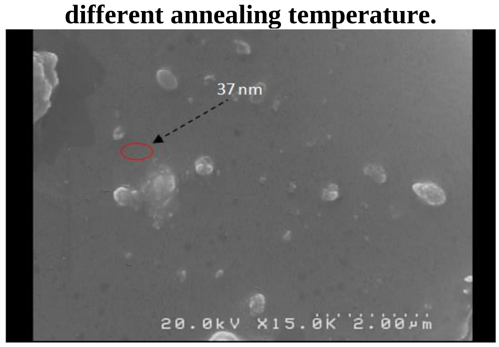


Figure 4. SEM for TiO_2 nanoparticles at different annealing temperature

The AFM technique uses a laterally moving tip, while the cantilever reflects the sample's topography, or the Z measurements. Even though the tip is very sharp, it is impossible to gather the information from the underside of specimen. The spherical particle will be viewed as a bump by the Atomic Force Microscope. To correct the AFM image for this effect some deconvolution techniques are used. In conclusion, the AFM and SEM images are complementing each other. Figure (4) shows the scanning electron microscope images of the TiO_2 films which consists of a uniform distribution of spherical shaped of nanostructured grains with a diameter of about (37 nm). This structure peats throughout the materials with closely packed to each other indicating good adhesiveness of film with the substrate.

The SEM study was carried out by VEGA TESCAN-SEM in University of Technology, Baghdad, Iraq at 20–30 kV. The reproducibility of structural, electrical and optical properties of porous silicon, that helps in device fabrication related to PSi. In this work, we stick to the optimum experimental parameters in respect of the PSi preparation with desired reproducibility. The porosity (gravimetric) values of the PSi layers formed on p-type Si wafers (henceforth, called as p-PSi) were 75 %, respectively, for an etching time of 15 min. The etching time has been fixed at 15 min with the current density of 25 mA/cm^2 as an optimum condition since the reproducibility of porosity values lies within 2–3 %. It is well known that PSi can exist in different microstructural forms depending upon various electrochemical parameters, silicon doping and resistivity. According to IUPAC classification of pore size, our PSi samples should belong to either the mesoporous (2–50 nm) or the nanoporous (\2 nm) region as evident from the plan-view SEM micrograph (Figure5).

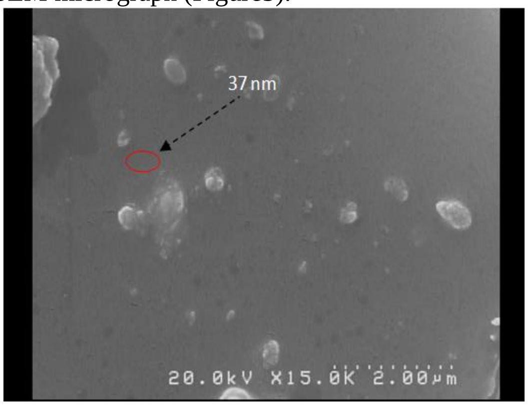


Figure 4. SEM for TiO_2 nanoparticles at different annealing temperature

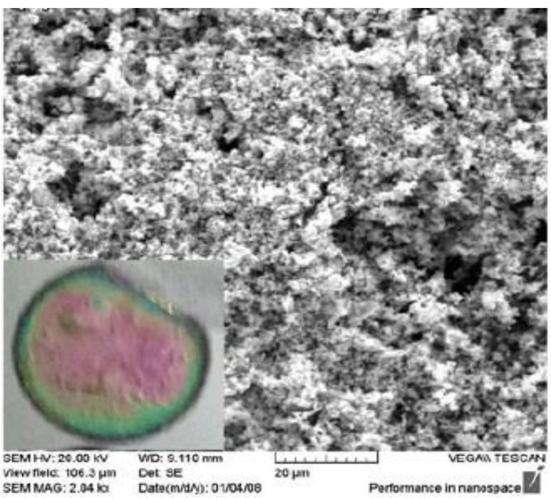
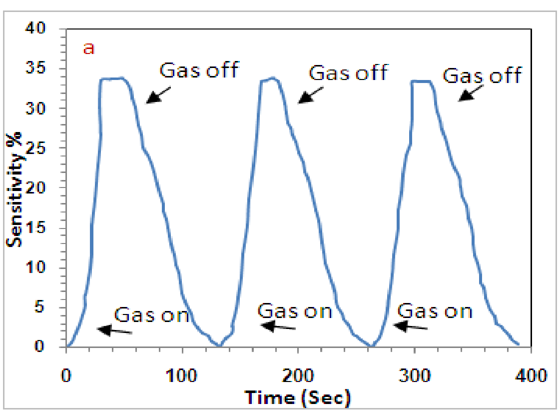


Figure 5. SEM for porous silicon used in this work



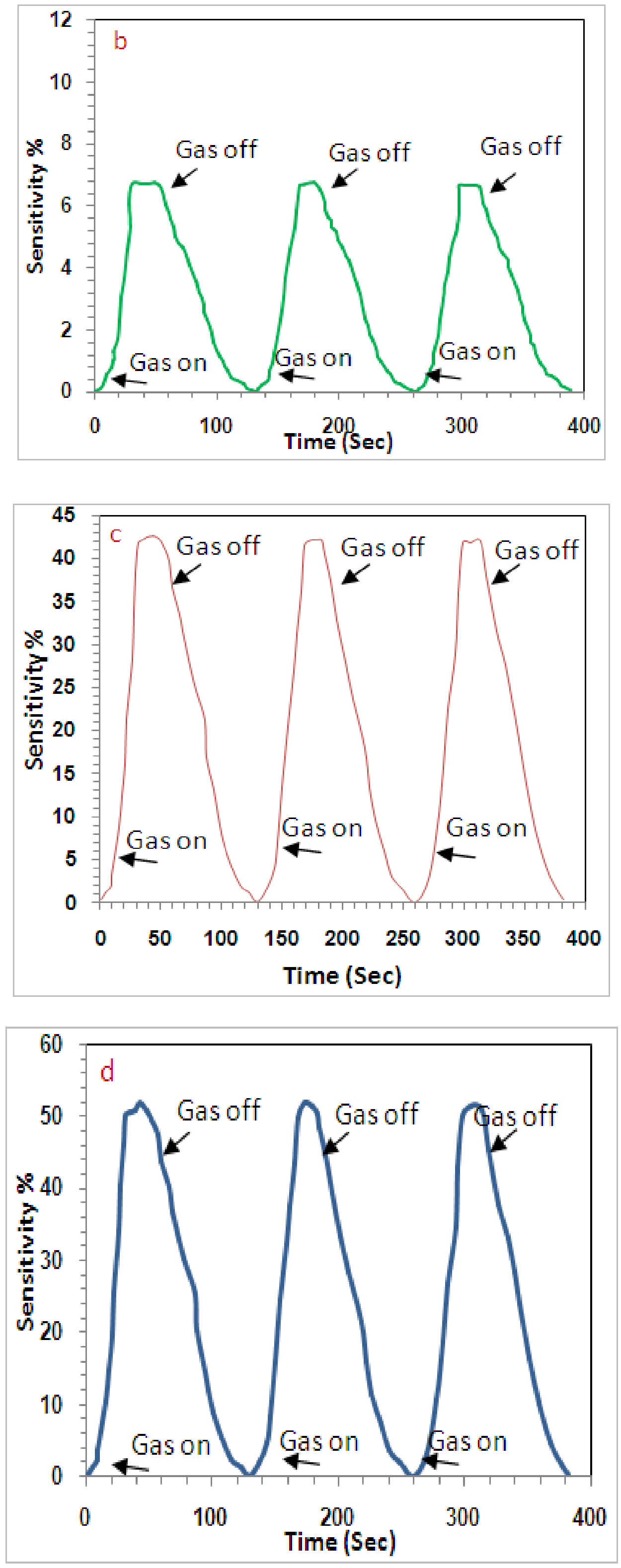


Figure 6. Variation of sensitivity with operating temperature

Figure (6) shows the typical response curve of the TiO_2nanopartical to 300 ppm vapor ethanol in dry air at the optimal operating temperature of 25^{o}C.The resistance of the TiO_2nano-partical sensors reduces with the presence of vapor ethanol. The reversible cycles of the response curve indicate a stable and repeatable operation of gas sensing. The response and recovery time are 150s, it is worth noting that the TiO_2 sensor shows an obvious response to various vapor ethanol concentrations even at room temperature 25 °C.

4. Conclusions

Titanium dioxide powder was prepared on p-type porous silicon by sol-gel process**.** The morphology of TiO_2 sensing film surface was imaged by atomic force microscope (AFM). The average roughness of the film surface is 25 nm**.** The X-ray diffraction (XRD) patterns shows of TiO_2nano-partical prepared by the solgel method are polycrystalline, the anatase phase with the preferential orientation of the crystallites along the [101] direction. The resistance of the TiO_2nano-partical sensors reduces with the presence of vapor ethanol.

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