Effect of thermal annealing on properties of polycrystalline Titanium dioxide (TiO$_2$) thin film prepared by simple chemical method

1Ali Hamid Abdulsada , 1Khudheir A. Mishjil , 2*Ahmad N. Abd

1Physics Department, Education College, Al-Mustansiriyah University, Baghdad, Iraq
2Physics Department, Science College, Al-Mustansiriyah University, Baghdad, Iraq
*Corresponding Email: ahmed_naji_abd@yahoo.com

Abstract: Titanium dioxide (TiO$_2$) thin film prepared in a simple chemical method, on an optically flat a glass substrate. The effect of the annealing temperature on a structural and the optical properties of TiO$_2$ films is studied systematically by X-ray diffraction (XRD), Atomic Force Microscopy (AFM), UV–VIS spectroscopy. The XRD patterns show that the deposited films and the annealed films are polycrystalline and the average grain size of the crystallite grains ranges from 41 to 50 nm in films. AFM images reveal a regular grain distribution of grains in films and the grains in the nanoscale dimension. The UV–Vis rays results show that increase in transmittance with increase the annealing temperature, also, the energy gap decreases from 3.6 to 2.6 volts, due to the effect of quantum volume.

Keywords: Titanium dioxide (TiO$_2$), Optical properties, FTIR, thermal annealing, AFM

1. Introduction

Titanium dioxide (TiO$_2$) is one of the important semiconductors that found in nature [1]. TiO$_2$ exist in three forms of Anatase, Rutile and Prokite [2] TiO$_2$ owned an energy band gap of (3.2 eV) and refractive index (n=2.52) [3]. It has a unique optical properties such as good magnetic properties [4] which has made the material important in many practical applications, including stimuli [5], energy conversion [6] and biomedical applications [7] functionalized hybrid materials [8] and nanocomposites [9]. TiO$_2$ can be used as solar cell applications (DSSC) [10] electrochemical cells (PEC) [11] chemical sensors [12] and self-cleaning coatings [13]. Thin films of TiO$_2$ are deposited by various methods including electron beam [14,15] magnetron sputtering technique [16], plasma evaporation [17], pulsed laser deposition [18], self-assembly process [19], laser chemical vapor depositing [20,21] and sol-gel method [22]. Ba-Abbad et al. (2012) synthesized the TiO$_2$ nanoparticles catalyst by sol-gel method using the titanium tetraisopropoxide as starting material. The effects of calcination temperatures on the crystalline structure, surface area and photo catalytic activity of TiO$_2$ nanoparticles were investigated. The anatase to rutile percentage decreases when temperatures are greater than 500°C and evaluated from XRD intensity of (101) and (110) peak, respectively [23].
Nocun et al. 2011 prepared SiO$_2$/TiO$_2$ thin films on glass and quartz substrates by dip coating sol-gel method. They showed that band energy gap ($E_g$) decreases with increase in TiO$_2$ content [24]. The aim of this work is to manufacture nanoparticles of titanium dioxide by a simple chemical method and Study structural, chemical and optical properties of titanium dioxide as a thin film deposited on glass substrate.

2. Experimental details
Titanium dioxide is fully prepared by Simple chemical method of 80 ml of water and adding 1 g of TiO$_2$ powder to heat the mixture at a temperature below boiling point 80 °C then tend add adrop (100μl) HF and PVC to speed up the interaction. The TiO$_2$ colloidal has been taken from the solution by pipette and then drop on the glass substrate only 5 drops, then waiting for (5-6 hours) until dry under room temperature.

3. Results and Discussion
Figure 1 depicts the x-ray diffraction pattern of TiO$_2$ thin films before and after annealing process. Several major peaks for as-prepared at 2θ = (25.2), (37.78) and (48) corresponding to (101), (004) and (200) respectively. The crystallite size were estimated using Sheerrer equation [29]

$$D_{av} = \frac{0.9 \lambda}{\beta \cos \theta} \ldots \ldots (1)$$

Where : $D_{av}$ The crystal size which measured by the nanometer, $\beta$ the full width at half maxima , $\theta$ is the angle of diffraction is measured by (deg) , where $\lambda$ (1.54056 Å) $\lambda$ is the wavelength of the incident X-ray. The crystallite size are found to be (41.5nm),(50.3nm) and (45.8nm). And the angle (25.28),(37.78) and (48.02) corresponds to (101),(004) and (200) after annealing. The crystallite size of TiO$_2$ thin films after annealing at 500 nm were (34.4nm),(46.4) and (41nm) respectively . Their values are listed in Table (1). These data were compared with JEPDS card number 021-1272, which refers to a hexagonal crystal structure. The process of annealing was not significantly affecting the material.

![Figure 1. X-ray pattern of TiO$_2$ film](image-url)
Both strain value and dislocation density can be calculated using the following equations (2) and (3), their values were listed in Table (1)

\[ \eta = \frac{\beta \cos \theta}{4} \ldots \ldots (2) \]

\[ \delta = \frac{1}{D_{av}} \ldots \ldots (3) \]

Figure (2) shows the 3D AFM image of TiO\(_2\) thin film deposited on glass substrate by drop casing method. The surface of the thin film has a vertically closely packed ball-shaped, homogenous and a good roughness grains of TiO\(_2\) nanostructure within scanning area (2×2)\(\mu\)m\(^2\) for as-prepared. The average diameter size, the roughness and the root mean square (RMS) was about (83.33nm), (0.267nm), (0.33nm) respectively and annealing at T=500C˚ the average diameter size, the roughness and the root mean square (RMS) were about (88.94nm), (10.3nm), (12.1nm) respectively.

![3D AFM image of synthesized TiO\(_2\) thin films](image-url)

**Figure 2.** 3D AFM image of synthesized TiO\(_2\) thin films
Table 1. the values of structural parameters of TiO$_2$ thin films before and after annealing

| Samples      | 2 Theta (deg) | hkl (Planes) | Beta (deg) | D (nm) | $\delta \times 10^{-3}$ | Strain $\times 10^{-3}$ |
|--------------|---------------|--------------|------------|--------|------------------------|------------------------|
| As-prepared  | 37.80         | (004)        | 0.166      | 50.333 | 3.9472                 | 6.8841                 |
|              | 48.04         | (200)        | 0.174      | 45.807 | 4.7657                 | 7.5642                 |
|              | 25.28         | (011)        | 0.235      | 34.461 | 8.4202                 | 10.054                 |
| Annealing at $T=500 \, ^{\circ}\mathrm{C}$ | 37.78         | (004)        | 0.180      | 46.415 | 4.6416                 | 7.6515                 |
|              | 48.02         | (200)        | 0.211      | 41.028 | 5.9407                 | 8.4454                 |

Figure 3 shows the FTIR spectrum of the compound TiO$_2$ powder. This indicates strong vibration of Ti=O about 687 cm$^{-1}$[32] . Absorption peaks around 3640 cm$^{-1}$ to 2500 cm$^{-1}$ due to the presence of O-H stretching vibration (monomer, intermolecular, intermolecular and polymer)[33] . The absorption band range at 1629 cm$^{-1}$ indicates the presence of O-H bending vibration. The Figure shows the (FT-IR) spectrum of as-synthesized TiO$_2$ thin films. In the case of film, the peak centered around 650 cm$^{-1}$ is due to the Ti=O extended vibrations [34]. The FT-IR spectra confirm the presence of Ti=O vibrations in both cases.
Figure (4) explains the transmittance spectrum of TiO₂ nanoparticles, from which it can be noticed that transmittance reaches 0.85 at 720 nm wavelength as shown in Fig 6-a and 0.24 at 720 nm at annealing at 500 °C as shown in Fig 4-b, then the transmittance increases as the wavelength increases.

![Transmittance Spectrum](image1.png)

**Figure 4.** Optical transmittance of TiO₂ thin films

Fig. (5) shows the variation of $(\alpha h\nu)^2$ versus $h\nu$ for direct band gap which have been determined by the extrapolation of linear portion versus the photon energy axis. It can be seen that the value of the energy gap is about 2.8 eV. The process of annealing affected the material and led to decrease in the value of energy gap to 3.6 eV, which may be attributed to quantum confinement as shown in Figure (5-a) and after annealing at 500 °C became 2.8 eV as shown in Figure (5-b).

![Band Gap Energy](image2.png)

**Figure 5.** $(\alpha h\nu)^2$ versus photon energy band gap for TiO₂ thin films

The reflectance of TiO₂ thin film increases from 0.35 to 0.47 when the wavelength increases from 380 nm to greater than 720 nm as shown in figure (6-a) and at annealing from 0.170 to 0.185 when the wavelength increases from 380 nm to greater than 720 nm as shown in figure (6-b).
Figure 6. Reflection spectra of TiO₂ thin film as a function of wavelength.

The refractive index (n) has been calculated by formula [35]:

\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \] \hspace{1cm} (4)

Figure 7 shows the change in the value of the refractive index as a function of the wavelength as in Figure (7-a), the index of refraction highest value is 1.65 at wavelength of 720 nm. Figure (7-b) Depicts the refractive index after annealing. The maximum value was 2.51 at a wavelength of 720 nm.

Figure 7. Refractive index spectra of TiO₂ thin film as a function of wavelength

Figure (8-a) shows black dots representing the gaps in this material. It is also clear to us from the pictures that the material is homogeneous and that its atoms are distributed equally on the surface of the base and it is clear to us that the atoms of the material in the form of spherical atoms and this is a confirmation of the tests of AFM where they give the same result. And that the effect of the process of annealing became the surface of the thin film more rough as shown in Figure (8-b) This is an important application of the material to act as a solar cell.
Figure 8. Optical microscopy images of TiO$_2$ nanoparticles:
(a) As-prepared (b) At annealing at 500 °C/h

Figure (9) shows the alternating current of the solar cell Al/TiO$_2$/Si/Al in two cases during preparation and at the annealing at 500 °C for one hour. It is observed from the curve that the behavior of the solar cell in the case of darkness takes a non-linear shape and is curved to an exponential function, which means that the mechanism of conductivity is not ohmic. In the forward bias, the current flows very freely and we observe a high value of the current. In reverse bias, the flow of current is very weak due to the flow of charge carriers and the applied voltage to inject the majority carriers and display the area of attrition. The concentration of the majority and minority carriers is higher than the concentration of the basic carriers, which generates the docking current in the region (0-0.2V). This is because the electrons are moved from the valence pack to the conduction beam and then returns to replace the gaps in the valence pack. Docking in the region is low voltage, while the tunnel condition occurs in the high voltage area and then we observe a huge increase in the value of the current with a small increase in voltage. This is called the propagation current which dominates the high voltage area. And in the case of the state of the deflection zone, the bias effort increases the width of the attenuation zone. This is why the concentration of the majority and minority carrier’s decreases and the current is increasing slightly by increasing the voltage.

Figure 9. shows the current-voltage curve in the dark for Al/TiO$_2$/Si/Al
The process of annealing greatly influenced the current-voltage scheme and from the figure we note that the current in the case of bias in the front became larger than after the material was born at 500°C within one hour because the process of dependence affected the material and made its particles to expand and increase the space between the gaps and leading to transit Bulk carriers and their transmission from the parity package to the delivery package.

The diagram (10) shows a current voltage diagram in the case of Al/TiO₂/Si/Al reverse bias in the case of darkness and in the case of lighting with a 15µW/cm² lamp and about 30cm away from the sample and studying its characteristics before and after the process of annealing at 500°C/h. It is clear to us that by means of the form, the optical current (I_{ph}) increases by increasing the rated voltage as well as increasing the intensity of the fall, thus increasing the number of charge carriers, as well as displaying the attrition zone increase with the increase of the reverse bias voltage, which leads to increased absorption and generation of electrons.

![Diagram 10](image_url)

**Figure 10.** Dark and illuminated (I-V) characteristic of Al/TiO₂/Si/Al Solar Cell (a) at as-prepared and (b) at annealing at 500°C/h

Figure 11 shows the voltage of the open circuit (V_{oc} , I=0 , R=∞), is the voltage output, as the load resistance is much greater than the device resistance. The short circuit current (I_{sc} , V=0 , R=0), is the current output when the load resistance is much smaller than the device impedance, then the Fill Factor (F.F) is the rate of maximum power output (V_{m} , I_{m}) respectively, to the product of V_{oc} and I_{sc} . From these parameters, efficiency can be estimated. The conversion efficiency (Ƞ) is defined as the ratio of (P_{m}/P_{in} ×100%) and F.F=(I_{m} V_{m}/I_{sc} V_{oc} ×100%) Calculated parameters of the solar cell for Al/TiO₂/Si/Al before and after the annealing process, tightness (15µW/cm²) are listed in Table (2) showing the estimated parameters of solar cell.

**Table 2.** Parameters of Solar Cell for TiO₂

| Sample            | V_{oc} (V) | I_{sc} (µA) | V_{m} (V) | I_{m} (µA) | F.F% | Ƞ% |
|-------------------|------------|-------------|-----------|------------|------|-----|
| As-Prepared       | 2.5        | 3.5         | 2.04      | 2.82       | 65.7 | 6.13|
| At annealing 500°C/h | 1.2        | 26.4        | 0.94      | 21.75      | 64.5 | 10.5|


Table (2) indicates when photons were incident on Al/TiO₂/Si/Al, We note that the value of the efficiency after the effect of the process of annealing, because after the process of annealing will show very thin layers on the surface of the sample and give it the ability to convert photons of light to greater electrical energy.

![Graph](image)

**Figure 11.** Open-circuit voltage of Al/TiO₂/Si/Al for (a) as prepared (b) at annealing at 500°C/h

4. Conclusions

The influence of the thermal annealing temperature on the crystalline structure, surface morphology and the optical properties of TiO₂ thin films were investigated. The XRD results have shown that the nanocrystalline TiO₂ films with preferred orientation along (101) direction can be observed before annealing and by increasing of annealing temperature to 500 °C no significant changes occur in the film structure. The TiO₂ phase and improvement of crystallinity was observed after annealing at temperatures of 500 °C. It was found that the annealing temperature significantly influenced the size and shape of the TiO₂ particles. The best crystallization, surface morphology and good absorption were observed at a temperature of 500 °C. Deposition of TiO₂ NPS on silicon gave suspensions Solar cell characteristics. The conversion efficiency (ƞ) of the solar cell for Al/TiO₂/Si/Al enhances after thermal annealing.

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