Research Article

Ahmed T. Hassan, Ehssan S. Hassan*, and Oday M. Abdulmunem

Effect of thermal annealing on the structural and optical properties of TiO$_2$ nanostructures**

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Abstract: In this work, TiO nanostructure films were deposited via vacuum thermal evaporation at a temperature of 80°C. The TiO thin films were annealed under vacuum for 1 h at three different degrees (200, 300, and 400°C) in addition to the thin film prepared at 80°C. X-ray Diffraction (XRD) showed that all the deposited and annealed TiO films had anatase polycrystalline diffraction patterns with a predominant reflection of the (200) plane. As a result, the particle size increased with annealing temperature. Scanning Electron Microscopy (SEM) measurements showed that at the annealed temperature of 200°C, the shape of the TiO nanostructures began to change from a condensed cluster distribution to a conical shape. As the annealing temperature was increased to 400°C, all the conical shapes transformed into clear spherical shapes. The spherical shapes recorded 45 (nm) height and (20) (nm) base width. Optical measurements were performed using Ultraviolet-Visible spectroscopy (UV-Vis). The transmittance is reduced from 79.63% for the TiO sample prepared at 80°C to 71.91% for the TiO sample annealed at 400°C. The optical energy gap values decrease from 3.279 eV for the prepared TiO sample at 80°C to 3.115 eV for the TiO sample annealed at 400°C.

Keywords: Titanium dioxide nanostructures, Thermal evaporation technique, Clusters like hemispherical

1 Introduction

Over the last 30 years, there has been extensive work focused on producing titanium oxide nanoparticles (TiO NPs) due to their low production cost, high efficiency [1], and use in a wide array of scientific applications such as photo electronic sensors [2]. Transition metal semiconductors, such as ZnO [3], CuO [4], SnO [5], and FeO [6], while titanium oxide is important because it has a wide energy gap of 3.0–3.6 eV, which makes it a compelling option for applications requiring a dielectric material. Titanium dioxide (TiO$_2$) is a negatively conductive n-type semiconductor material due to intrinsic defects in the crystal structure of the lattice [7].

Titanium dioxide can be present in multiple crystal phases, such as anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [8]. It can also exist in an amorphous solid state. The anatase phase has an energy gap of 3.0 eV – 3.2 eV, and its electrons are high mobility, making it suitable for photocatalytic and antibacterial applications [9]. This phase is also stable at high temperatures. The rutile phase has an energy gap of 3.2 eV – 3.4 eV.

TiO NPs can be produced by multiple methods, including sol-gel [10], Direct Current (DC) sputtering and Radio Frequency (RF) sputtering [11], thermal evaporation [12], and spray pyrolysis [13–16]. In the present research, TiO films were produced through thermal evaporation, where TiO was used in the form of powder, and the evaporation boat was composed of molybdenum. The novelty of this research lies in examining the relationship between the annealing temperature and the resulting titanium oxide nanostructures Thus, we can determine different applications depending on the resulting nanostructures.

2 Materials and methods

Titanium oxide powder with a purity of 99.99% was placed in a molybdenum boat to prepare titanium oxide films by thermal evaporation. An increase in the current (0-300 Amp) raised the temperature almost about (0.26°C/W) inside the chamber leading to increase the pressure in the
vacuum chamber = $(1 \times 10^{-5} - 1 \times 10^{-2}$ mbar). The material was deposited on the surface of the glass substrate, which was installed at 15 cm away from the evaporation boat at an angle of $\theta = 30^\circ$. Further, a deposition rate of $2 \text{ (nm)} \cdot \text{s}^{-1}$ was used.

### 3 Results and discussion

Figure 1 shows the XRD patterns of titanium oxide prepared by thermal evaporation under vacuum at a temperature of $80^\circ \text{C}$ (as deposited) and those for the samples annealed at 200, 300, and $400^\circ \text{C}$ for 1 h. In Figure 1, the matching diffraction pattern for all TiO samples is anatase polycrystalline identical to the international card 43-1269, with a predominant reflection of the (200) plane at $2\theta = 43.57^\circ$. The intensity of the reflection increases with increased annealing temperature as can be seen from Figure 1(a). The relationship of the full width at half maximum (FWHM) with the annealing temperature for all samples decreases with increased annealing temperature. This indicates an increase in the crystallite size [17], as shown in Figure 2(a). The calculation of the FWHM was done using Origin graphing software. The crystallite size was calculated using the Debye-Scherer equation. The values of the FWHM and the crystallite size have been recorded in Table 1. Figures 2(c and d) present the macrostrain and the dislocation density as a function of annealing temperatures [18].

Several secondary reflections of the planes (111), (220), (311), (222) and (400) correspond to $2\theta = 37.40^\circ$, $62.70^\circ$, $75.13^\circ$, $79.37^\circ$ and $94.28^\circ$.

The macrostrain and dislocation density values decrease with increased annealing temperature because of the increase in crystallization and the decrease in crystal defects, macrostrain and the dislocation density values recorded in Table 1.

Figures 3(a, b, c, and d) depict the SEM micrographs of samples (as deposited, 200, 300, and $400^\circ \text{C}$) for 1 h. Figures 3(a1, b1, c1, and d1) are the schematics of the grain growth samples of titanium dioxide prepared by thermal

| Annealing T. $^\circ \text{C}$ | (hkl) plane | $2\theta$ [°] | FWHM (deg.) | Crystallite size (nm) | Micro strain | Dislocation density $(1/\text{m}^2) \times 10^{14}$ |
|-------------------------------|-------------|-------------|-------------|----------------------|-------------|----------------------------------|
| 80                            | (200)       | 30.12       | 0.415       | 16.89                | 9.843       | 10.483                           |
| 200                           | (200)       | 43.87       | 0.314       | 17.36                | 17.481      | 33.064                           |
| 300                           | (200)       | 43.29       | 0.236       | 17.39                | 17.505      | 33.155                           |
| 400                           | (200)       | 43.75       | 0.221       | 30.88                | 17.992      | 35.027                           |
Figure 3: SEM images and schematic grain of TiO (a and a1) at 80°C (as deposited), (b and b1) at 200°C, (c and c1) at 300°C and (d and d1) at 400°C.
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Figure 4: (a and b) The transmittance and absorbance spectra, respectively, as a function of the wavelength, (c) $(\alpha h \nu)^2$ as a function of the photon energy of TiO at different annealing temperatures.

Evaporation under vacuum at a temperature of 80°C (as deposited), and for samples annealed at 200, 300, and 400°C for 1 h. From the initiation of the film deposition on the surface of the substrate at 80°C, the first nuclei begin to form as clusters with a homogeneous surface due to the low temperature as shown in Figures 3(a) and 3(a1). Figures 3(b) and 3(b1) represent the increase in annealing to 200°C, which is considered low temperature. The nuclei combine with their neighbours to form condensed clusters within a homogeneous layer. This is due to the availability of sufficient thermal energy to move these particles and increase the surface energy of the preferred reflection (200), which makes the atoms cluster together. Figures 3(c) and 3(c1) show that with the increase of the annealing temperature to 300°C, the size of these grains increased, and the shape of the nanostructures changed from a condensed cluster distribution to a conical structure. Figures 3(d) and 3(d1) show TiO films annealed at 400°C, in which all the conical shapes are transformed into spherical shapes because of the re-evaporation of the deposited atoms with the increased annealing temperature.

Figures 4(a and b) presents the transmittance and absorbance spectrum as a function of the wavelength of titanium oxide prepared by thermal evaporation under vacuum at a temperature of 80°C (as deposited) and the samples annealed at 200, 300, and 400°C for 1 h. The transmittance is reduced from 79.63% for the sample prepared at 80°C to 71.91% for the sample annealed at 400°C, this can be attributed to the increase in the crystallite size reducing the grain boundaries. Consequently, the scattering of the incident rays is reduced. The transmittance was measured in the near-infrared region, making the annealed samples useful as an infrared window at wavelengths of 700–875 nm.

Figure 4(c) presents the optical energy gap values for titanium oxide prepared by thermal evaporation under vacuum at a temperature of 80°C (as deposited) and the samples annealed at 200, 300, and 400°C for 1 h. The optical energy gap values decrease from 3.279 eV for the prepared sample at 80°C to 3.115 eV for the sample annealed at 400°C.

The optical energy gap can be estimated by plotting $(\alpha h \nu)^2$ vs $h \nu$ and then extrapolating the linear portion of the plot to the photon energy axis. Here, all values can be linked, as changing the particle size and the nanostructures influence the optical properties. Note that the increase in annealing temperature led to an increase in the clusters of atoms due to the increase in surface energy, and thus a decrease in the transmittance spectrum. This is made clear by the decrease in the energy gap values [18].

4 Conclusions

In the present work, titanium oxide was deposited in the TiO phase using the thermal evaporation method. Structural measurements of the as-deposited sample prepared at 80°C and the annealed samples at 200, 300, and 400°C show polycrystalline anatase structures. A single orientation in the (200) plane dominates for all samples, and the grain size increases from 16.89 to 30.88 (nm) with increased annealing temperature. Hemispherical and spherical nanostructures with a base length of 20 (nm) and a height of 45 (nm) emerge with increased annealing temperature, and the propagation of these nanostructures is uniform over the entire area measured. The transmittance decreases from 79.63% to 71.91%, and the energy gap value decreases from...
3.279 eV to 3.115 eV when the annealing temperature is increased. We conclude that increasing the annealing temperature can change the shape of the nanostructures formed on the surface, which allows tailoring the properties of TiO\(_2\) towards wider applications.

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**Author Contributions:** Ahmed T. Hassan, Ehssan S. Hassan and Oday M. Abdulmunem conceptualized the topic, tested the samples and approved the final manuscript.

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