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Phase Evolution and Optical Response of TiO_2 Nanoparticle Films Induced by Controlled Thermal Annealing

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Abstract: This study investigates the influence of annealing temperature on the structural, photoluminescence, and optical properties of TiO_2 nanoparticle thin films fabricated by thermal oxidation of titanium thin films deposited using electron-beam evaporation. Structural analysis was performed using X-ray diffraction (XRD), while optical and luminescence behavior were studied using UV–Vis transmittance and photoluminescence (PL) spectroscopy. The results revealed clear phase transitions influenced by annealing temperature: anatase phase appeared at low (100 °C) and high (500 °C) temperatures, rutile emerged at 200–300 °C, and brookite was identified at 400 °C. These phase changes strongly impacted the optical band gap and PL emission. A red-shift in PL peaks with increasing temperature indicated nanoparticle growth, while the weakest PL signal was associated with brookite formation. The anatase-rich samples showed higher band gaps and stronger PL intensity, confirming a strong correlation between structural phase and optoelectronic performance. These findings demonstrate the critical role of thermal treatment in tailoring TiO_2 thin films for advanced applications.

Keywords: TiO_2 NPs; Annealing; Electron beam deposition; Anatase; Rutile.

1. Introduction

Titanium dioxide has three main crystalline structures: anatase, rutile, and brookite, in addition to the amorphous phase [1]. It is one of the transition metal oxides that has received a wide study [2] due to its photochemical stability and optical activity, in addition to its non-toxicity. In addition, it has many structural and mechanical properties such as chemical stability, good adhesion, and high stability against mechanical corrosion and high temperatures [3]. In addition to all of this, its low manufacturing cost [4]. All of these features make titanium dioxide suitable for many important applications such as solar cells, gas sensors, air and water purification, and water treatment [5,6], and it is also used in the manufacture of positive electrodes for lithium-ion batteries, self-cleaning glasses [7], cosmetics [8], and anti-reflective coatings [9].

Many deposition methods have been used to synthesize TiO_2 NPs thin films, including physical methods such as DC or RF magnetic sputtering [10], thermal evaporation [1], electron beam evaporation [11], and pulsed laser deposition (PLD) [12]. In addition, some chemical methods are also used to prepare this oxide such as spin coating of sol-gel precursors [8], and chemical vapor deposition (CVD) [13].

In this work, we highlight the possibility of investigating specific phase transitions induced by thermal annealing of titanium oxide thin films by studying the relationship between the relative intensities of features appearing in the luminescence spectra and the energy band gap.

2. Experimental

2.1. Sample preparation

Pure Ti thin films were deposited at room temperature on to thoroughly cleaned n-type Si (100) and glass substrates from a high-purity Ti (99.99%) target by using electron-beam evaporation method. The substrate placed below the source in the direction of ablated material flux. The deposition conditions are given in table 1.

Table 1: The deposition parameters during titanium thin films preparation process.

Deposition parameters	
Vacuum pressure	5.0×10^{-6}mbar
Emission current intensity	20.0 mA
Operating voltage	4600.0 V
Substrate - target distance	50.0 cm
Duration of the deposition process	3.0 hour
Film thickness	140.0 Aº

Each deposited film was annealed in air at specific temperature (100, 200, 300, 400 and 500 °C) in order to oxidize the titanium atoms and obtain TiO_2 NPs thin films. Table 1 contains the thermal treatment conditions for each sample.

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Table 2: The thermal treatment conditions for each sample.

Sample code	Temperature(°C)	Processing time (hr)
A	100.0	1
B	200.0	1
C	300.0	1
D	400.0	1
E	500.0	1

2.2. Sample characterization

The optical transmittance spectra of the prepared films were recorded with a UV–Vis spectrophotometer (Cary 5000). The photoluminescence (PL) spectra were recorded at room temperature using a He–Cd laser with an excitation wavelength of 325 nm. The crystallite structure of the films was measured by X-ray diffraction (XRD) using Philips compact X-ray Diftractmeter System PW 1840 employing a Cu $K\alpha_1$ ($\lambda = 1.54060$ Å) source.

3. Results and discussion

The crystalline phase composition of the annealed TiO_2 thin films was analyzed by X-ray diffraction (XRD). The XRD profiles of these samples are shown in Fig. 1. Distinct phase transitions were observed as a function of annealing temperature: At 100°C (Sample A), the dominant diffraction peak at 25.3° corresponds to the (101) plane of the anatase phase (JCPDS 21-1272). At 200°C (Sample B), a prominent peak at 27.4° is indicative of the (110) plane of the rutile phase (JCPDS 21-1276). At 300°C (Sample C), both anatase and rutile peaks appear, showing a mixed-phase composition. At 400°C (Sample D), a clear peak at 30.8° reflects the presence of the brookite phase (JCPDS 29-1360). At 500°C (Sample E), anatase phase dominates again with sharper peaks, indicating improved crystallinity and grain growth. These results confirm that annealing temperature has a significant influence on the phase evolution of TiO_2, consistent with thermally activated nucleation and transformation mechanisms.

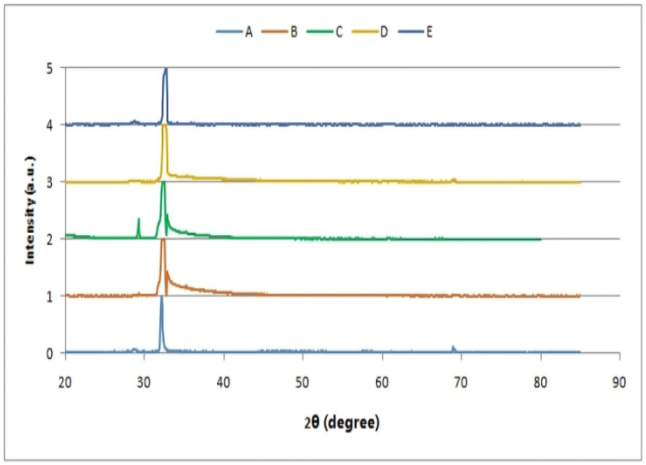

Fig. 1: The XRD spectra of the prepared samples.

Figure 2 shows the effect of annealing temperature on the transmittance spectra of the prepared samples. Samples (A) and (D) show lower transmittance in the visible light range compared to the other samples, which can be explained by the lower oxidation rate in these two samples.

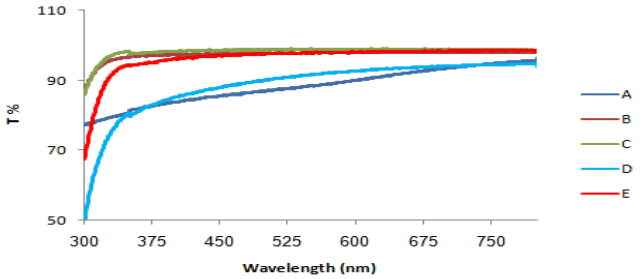

Fig. 2: Transmittance spectra of the prepared thin films.

Optical transmittance spectra were used to calculate the energy band gap (Tauc gap) for all samples. The band gap is calculated using the equation [14]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^{0.5} \quad (2)$$

Where $h\upsilon$ is the energy of the incident light and E_g is the estimate of the band gap and **A** is a constant. Fig. 3 shows the energy band gap as a function of annealing temperature. The energy band gap values range from 3.05 to 3. eV. Sample A has the lowest energy band gap value (3.05 eV) due to its richness in titanium, which causes a decrease in the electrical conductivity of the film.

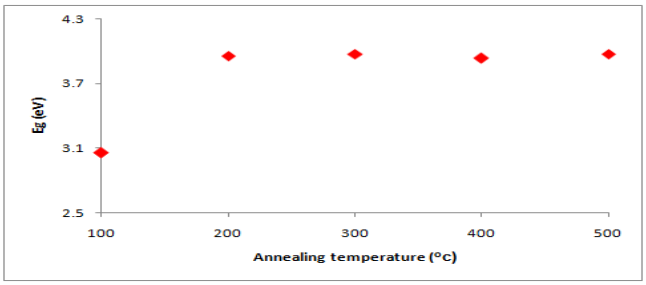

Fig. 3: The energy band gap as a function of annealing temperature.

Figure 4 shows the PL spectra of the as-prepared samples. Clear luminescence signals are observed, with a maximum intensity at 438 nm, resulting from the presence of titanium oxide nanoparticles [15]. These peaks are symmetrical, and it can be seen that the luminescence intensity (peak area) decreases with increasing annealing temperature in the range of 100–400 °C, and then increases significantly at an annealing temperature of 500 °C (sample E). The luminescence peak almost disappears in the case of the sample treated at 400 °C (sample D).

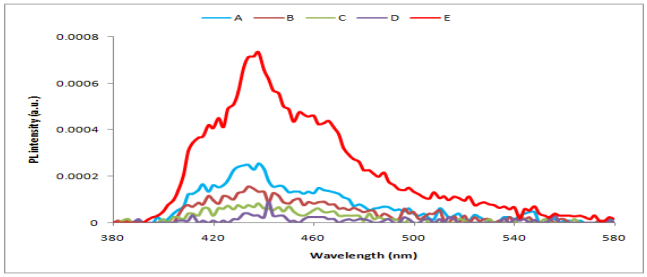

Fig. 4: The PL spectra of the prepared Ag_2O thin films.

In order to investigate the overlapping peaks in Fig. 3, each spectrum was deconvoluted into two Gaussian–Lorentzian line shapes (peak1 and peak2). Fig. 5 shows example of the deconvolution processes that concern the case of sample A that treated at 100 °C. The appearance of the tow peaks is due to the presence of multiple energy levels of the mixed phase (anatase and rutile) [15].

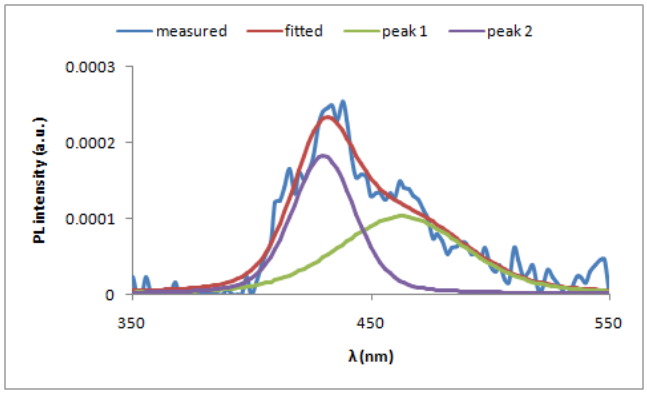

Fig. 5: Example of the deconvolution processes that concern the curve of sample A.

Fig. 6 shows the positions of peak1 and peak2 as functions of annealing temperature. We notice that increasing the annealing temperature results in a red-shift of the peak, indicating an increase in the size of the titanium oxide nanoparticles [15]. Sample D deviates from this behavior, as annealing at 400°C leads to a shift of the peaks towards lower wavelengths due to the decline in thermal oxidation in this case.

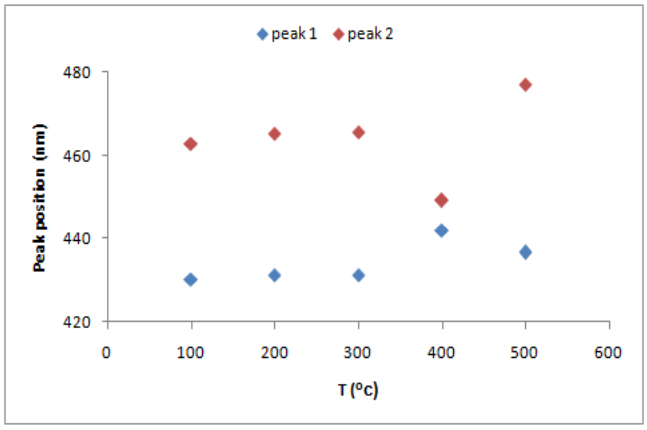

Fig. 6: The peak position as a function of annealing temperature.

Fig. 7 shows the M ratio as a function of the energy band gap. The M ratios represent the ratio of the peak area 1 to the peak area 2. We notice that, with the exception of Sample A, which has a high titanium content, the M ratio increases as the energy band gap value increases. This means that the intensity of peak 1 increases as the film conductivity decreases. This result indicates that the anatase phase enhances as the film conductivity decreases because it has a higher energy band gap than that of the rutile phase.

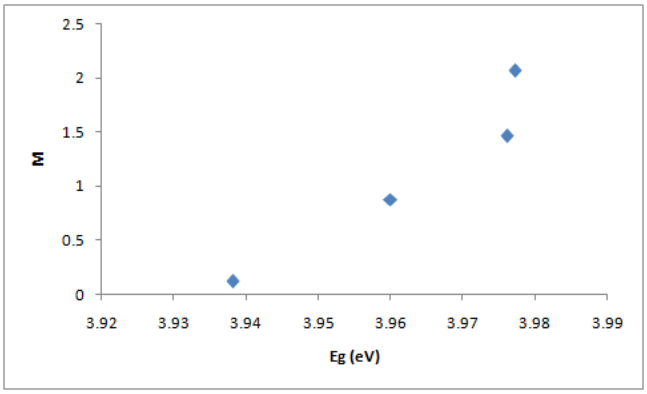

Fig. 7: The M ratio as a function of the energy band gap.

These observations are in good agreement with the XRD results, which confirmed the dominance of the anatase phase in samples annealed at 100 °C and 500 °C—corresponding to higher M ratios and energy band gaps. Conversely, rutile-related peaks observed in XRD for samples annealed at 200–300 °C are consistent with lower M ratios and reduced band gaps. Furthermore, the significant drop in PL intensity for sample D aligns with XRD evidence for brookite formation, a phase known to have weaker optical activity. This correlation highlights the strong interplay between crystalline phase transitions and optical/luminescence behavior in thermally treated TiO_2 thin films.

4. Conclusions

In this work, we investigated the effect of annealing temperature on the structural, photoluminescence, and optical properties of TiO_2 nanoparticle thin films synthesized via thermal oxidation of titanium layers deposited by electron-beam evaporation. Based on the analysis of XRD patterns, transmittance spectra, and PL emission, the following conclusions can be drawn:

1. X-ray diffraction (XRD) analysis confirmed that annealing temperature strongly influences the phase composition of TiO_2 films, with anatase dominating at low (100°C) and high (500°C) temperatures, rutile appearing at 200–300°C, and brookite forming at 400°C.
2. Photoluminescence and optical transmittance spectra were significantly affected by the annealing

temperature, reflecting the changes in crystal phase and nanoparticle size.

3. The lowest energy band gap (3.05 eV) was observed in sample A, due to incomplete oxidation and high titanium content, while higher band gap values corresponded to anatase-rich samples.
4. Increasing the annealing temperature led to a red-shift in PL peaks, indicating growth in nanoparticle size. Anomalies such as weak PL in sample D are attributed to brookite formation and insufficient oxidation.
5. A clear correlation was established between phase composition (from XRD), optical band gap, and photoluminescence behavior, supporting the structure–property relationship in TiO_2 thin films.

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