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Influence of Thermal Annealing on the Band-Gap of TiO_2 Thin Films Produced by the Sol-Gel Method

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ABSTRACT

In our study, we used the spin coating method to produce TiO_2 thin films on quartz glass using a solution with a concentration of 0.5M. After the coating process, the samples were dried in air at 100°C. Subsequently, annealing was carried out at four different temperatures, namely 300°C, 500°C, 700°C, and 900°C, for a duration of 60 minutes. Comprehensive analyzes including Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-ray Diffraction (XRD) and optical measurements were carried out to investigate the structural and optical properties of the samples. Optical measurements showed that the highest average transmittance values were obtained for samples annealed at 300°C and 500°C, with percentages of 82.33% and 80.25%, respectively. Remarkably, the maximum transmittance of 99.58% was recorded for films annealed at 500°C. Additionally, band-gap calculations were performed using the Tauc method based on optical measurements of samples exposed to different annealing temperatures. According to our results, samples annealed at 300°C, 500°C, 700°C, and 900°C exhibited band-gap values of 3.42eV, 3.40eV, 3.38eV, and 3.29eV, respectively.

Keywords: TiO_2 Thin film, sol-gel, band-gap, thermal annealing

Sol-Jel Yöntemiyle Üretilen TiO_2 İnce Filmlerinin Bant Aralığı Üzerinde Termal Tavlamanın Etkisi

ÖZ

Çalışmamızda, 0,5M konsantrasyonlu bir çözelti kullanarak kuvars cam üzerine TiO_2 ince filmler üretmek için spin kaplama yöntemini kullandık. Kaplama işleminden sonra, örnekler kurulama için hava ortamında 100°C'de ısıl işleme tabi tutuldu. Daha sonra, 300°C, 500°C, 700°C ve 900°C olmak üzere dört farklı sıcaklıkta, 60 dakika boyunca tavlama işlemi gerçekleştirildi. Üretilen örnekler, yapısal ve optik özelliklerini incelemek amacıyla kapsamlı analizlere tabi tutuldu, bu analizler arasında Taramalı Elektron Mikroskobu (SEM), Enerji Dağılım Spektroskopisi (EDS), X-ışını Kırınımı (XRD) ve optik ölçümler yer almaktadır. Optik ölçümler, 300°C ve 500°C'de tavlanan örnekler için sırasıyla %82,33 ve %80,25 olan en yüksek ortalama geçirgenlik değerlerinin elde edildiğini gösterdi. Dikkat çekici bir şekilde, 500°C'de tavlanan filmler için %99,58'lik maksimum geçirgenlik kaydedildi. Ayrıca, farklı tavlama sıcaklıklarına maruz kalan örneklerin optik ölçümlerine dayanarak Tauc yöntemi ile band-gap hesaplamaları yapıldı. Bulgularımıza göre, sırasıyla 300°C, 500°C, 700°C ve 900°C'de tavlanan örnekler için, 3,42eV, 3,40eV, 3,38eV ve 3,29eV bant aralığı değerleri elde edildi.

Anahtar Kelimeler: TiO_2 ince film, sol-jel, bant aralığı, termal tavlama

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1. Introduction

The thin films of Titanium dioxide (TiO_2) exhibit a broad potential for use in optoelectronic and photocatalytic applications. The band-gap value, a critical measure determining the electronic structure of the material, is one of the physical properties of these thin films. Thermal annealing can have significant effects on the band-gap values of TiO_2 thin films (Hasan et al., 2008). Generally, the thermal annealing process at high temperatures contributes to the rearrangement of the crystal structure and induces changes in the band structure by influencing the atomic arrangement. Specifically, the high temperatures during thermal annealing can rectify crystal defects in the thin film and optimize the arrangement of atoms (Amin et al., 2013, Vadas et al., 2020). This process can induce changes in the band structure by affecting the energy levels of electrons. As a result of thermal annealing, a typically observed change is in the band-gap value, signifying a significant evolution in the electronic properties of the material. It is evident that these thermal processes represent an important research topic aimed at optimizing the performance of TiO_2 thin films in applications such as solar cells, sensors, and photocatalysis (Garzella et al., 2000, Lu et al., 2003, Andronic and Duta 2007). Changes in band-gap values enable the development of strategies aimed at achieving improved performance in a variety of applications by influencing the light absorption, transport and reaction properties of the material. TiO_2 is a compound that exhibits three different crystal structures: these are the anatase, rutile, and brookite phases. Among these phases, the rutile phase is thermodynamically the most stable and dense. The anatase phase, on the other hand, has a semi-stable character at temperatures below 600°C and undergoes transformation over time into the rutile phase (Wen et al., 2001, Stevanovic and Yates Jr 2013). Although both the anatase and rutile phases have a tetragonal crystal structure, the brookite phase has an orthorhombic structure. In particular, the stability and density of the rutile phase hold significant importance in various industrial applications and materials science (Gupta et al., 2013). The understanding of these distinct crystal structures is crucial for optimizing the performance of TiO_2 in various industrial applications and contributing to materials science. In this context, the thermal transformations of the crystal structures and their effects on the material properties emerge as a significant topic requiring advanced research and analysis. In this study, TiO_2 thin films were deposited on Quartz glass using the sol-gel method. The films were then annealed in air at four different temperatures, 300°C, 500°C, 700°C and 900°C for 60 minutes. TiO_2 thin films produced at different annealing temperatures were thoroughly examined using various characterization techniques such as XRD, SEM, EDS, and optical properties. Following these characterizations, band gap values for each temperature were calculated using the Tauc method based on the analysis of optical properties. This study is innovative in terms of examining the relationship between annealing temperature and band-gap values. Thus, based on the results, different application areas can be determined according to the band-gap values.

2. Material and Method

In the preparation process of TiO_2 thin films, Titanium (IV) isopropoxide (97% purity, Sigma Aldrich) was used as the TiO_2 source, and ethyl alcohol along with distilled water were chosen as the solvents for TiO_2 precursor solutions. Quartz glass substrates measuring 1cm×1cm were preferred for optical measurements. Quartz glass substrates were cleaned in an ultrasonic bath with acetone, ethyl alcohol, and water for 5 minutes. After the cleaning, a 0.5M TiO_2 solution was prepared, and the coating process was carried out by dropping 50 µl of this solution onto the substrates (Kanmaz and Tomakin 2023). The coating process was conducted at a speed of 2500rpm. All samples were dried at 100°C for 5 minutes and subsequently subjected to annealing in air at 500°C (Figure 1). XRD patterns in the range of 20°-60° were obtained using a Rigaku Smartlab diffractometer to examine the crystal structures of the thin films. Morphological features were investigated using a Zeiss EVO LS10 scanning electron microscope (SEM) with an acceleration voltage of 10 kV. Optical measurements, such as transmittance and absorbance, were performed using the SpectraMax M5 UV-Vis spectrophotometer.

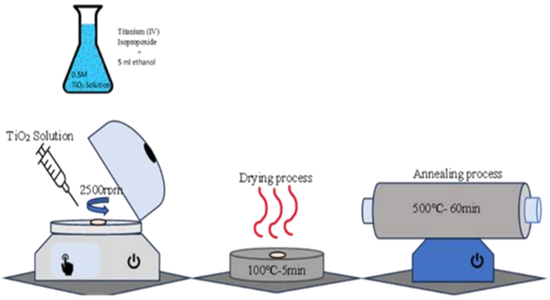

Figure 1. Production stages of TiO_2 thin films with spin coating

3. Result and Discussion

It is known from the literature that the annealing process is effective on the optical, structural and electrical properties of thin films (Modreanu et al., 2006, Mahmood et al., 2010). In our study, in order to investigate the effect of annealing temperature on the band-gap values of TiO_2 thin films, optical measurements were carried out by annealing in air at four different temperatures, 300°C, 500°C, 700°C and 900°C, after coating 0.5M TiO_2 thin films on the quartz glass surface. Optical measurements included transmittance and absorbance graphs for TiO_2 thin films at different annealing temperatures, as shown in Figure 2. The average, maximum, and minimum transmittance values for each sample were calculated from the transmittance graphs, and these values are summarized in Table 1. With the increase in the annealing temperature, it was observed that the maximum transmittance point shifted to low wavelengths and there was a decrease in the maximum transmittance values.

A similar situation was observed with respect to in absorbance values. As the annealing temperature increased, the minimum absorbance point shifted to lower wavelengths. However, it was observed that the mean transmittance values decreased with the increase in annealing temperature. For example, the highest average transmittance values were obtained for 300°C and 500°C as 82.33% and 80.25%, respectively.

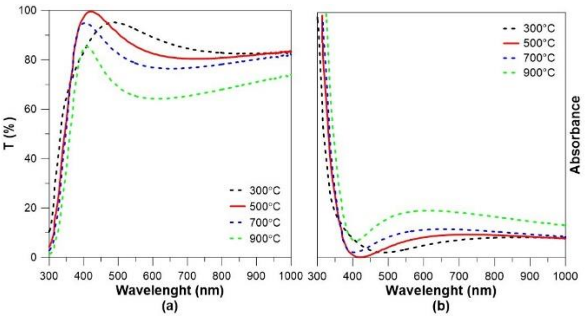

Figure 2. The transmittance (a) and absorbance (b) graphs depend on thermal annealing of TiO_2 thin films

The annealing temperature with the highest maximum permeability was determined as 500°C. This indicates that the annealing process at 500°C significantly improves the crystal structure and molecular ordering of the TiO_2 thin film. This improvement allows light to pass through the thin film with less hindrance, resulting in high transmittance.

Table 1. Transmittance values at different annealing temperatures

Temperature (°C)	Average T(%)	Minimum T(%)	Maximum T(%)
300	82.33	10.45	95.21
500	80.25	04.27	99.58
700	76.27	02.78	95.03
900	65.12	01.41	85.50

Similarly, an increase in the annealing temperature leads to a decrease in transmittance and an increase in absorbance. This suggests that annealing at higher temperatures induces more crystal degradation or structural defects in the TiO_2 thin film. These defects impede the passage of light, thereby reducing transmittance, while simultaneously enhancing light absorption, leading to increased absorbance. Figure 3(a) shows the average transmittance values, while Figure 3(b) shows the maximum transmittance values along with their corresponding annealing temperatures.

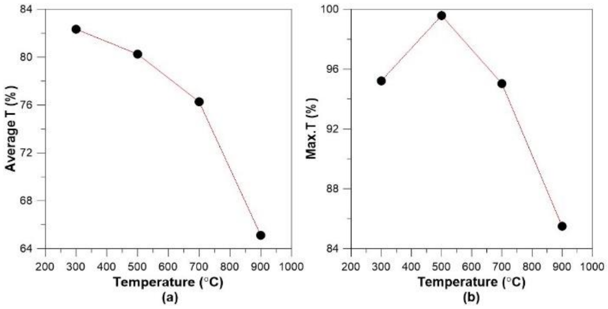

Figure 3. Average (a) and Maximum (b) Transmittance values depending on the annealing temperature

As shown in Figure 3(a), an increase in annealing temperature results in a decrease in the average transmittance values. Furthermore, as shown in Figure 3(b), the maximum transmittance value is achieved at an annealing temperature of 500°C. Additionally, by utilizing the optical spectrum of the thin films, band-gap calculations can be performed using the Tauc method (Tanemura et al., 2005). This method attempts to determine the band gap energy of a material by utilizing the relationship between the wavelength and absorption coefficient of its absorption spectrum. This relationship is expressed by the Tauc equation, given in eq (1).

$$\alpha h\nu=\beta(h\nu-Eg)^n \quad (1)$$

where α represents the absorption coefficient of the material, hν denotes the photon energy, Eg represents the optical band gap, β is a constant known as the band tailing parameter, and n is a power factor dependent on the type of optical transitions (direct~1/2 or indirect-2) (Pawlak and Al-Ani 2019, Surah et al., 2019). Additionally, the absorption coefficient α (cm^{-1}) of the films was determined using eq (2).

$$\alpha=\frac{1}{d}\ln(\frac{1}{T}) \quad (2)$$

where, d is the thickness of the thin film, and T is the transmittance. The Tauc method is used to determine the optical band gap (Eg) of a material by measuring the absorption spectrum at different wavelengths and fitting a straight line that conforms to the Tauc equation

The point where this line intersects the x-axis provides the value of the optical band gap (Dolgonos et al., 2016, Baishya et al., 2018). Figure 4 shows the band gap values of TiO_2 thin films obtained at different annealing temperatures using the Tauc equations. the thickness value of the film cross-sections was measured to be in the range of 60-65nm through by SEM measurements.

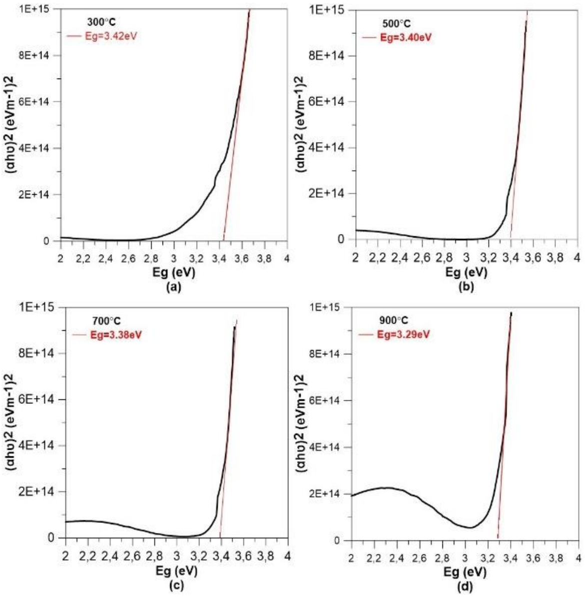

Figure 4. The effect of various thermal annealing temperatures, including (a) 300°C, (b) 500°C, (c) 700°C and (d) 900°C on the band gap of TiO_2 thin films

Bandgap calculations were performed for samples annealed at different temperatures, including 300°C, 500°C, 700°C and 900°C. The outcomes of these calculations revealed interesting trends in the material's electronic properties. For the sample annealed at 300°C, the calculated band gap value was determined to be 3.42 eV. As the annealing temperature was increased, a systematic reduction in the band-gap values was observed. The band gap decreased to 3.40 eV for the sample annealed at 500°C, further declining to 3.38eV at 700°C, and reaching 3.29 eV for the sample annealed at 900°C. This observed trend indicates a notable influence of the annealing temperature on the band gap of the TiO_2 thin films. The decrease in band-gap values with increasing annealing temperature may be indicative of changes in the material's crystalline structure or electronic configuration. 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 (Hassan et al., 2022). The fact that the ban-gap values of TiO_2 thin films can be adjusted with annealing temperature can create a wide range of uses of TiO_2 thin films in electronic and optoelectronic devices such as solar cells, transistors, diodes, etc. In addition, XRD and SEM images of samples at 500°C annealing temperature, where maximum transmittance occurs, were examined. XRD measurements were performed to determine the crystal orientation and crystallinity status of the thin films, and the results of these measurements are given in figure 5.

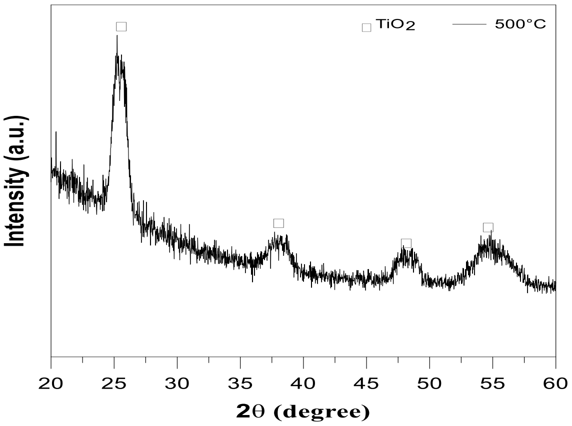

Figure 5. X-ray Diffraction (XRD) patterns of TiO_2 thin films at 500°C

It was determined that TiO_2 thin film grew in the anatase phase and that the four main peaks belonged to TiO_2 thin films. These peaks were observed to grow in planes (101), (004), (200) and (211), respectively. Also, SEM analyses of the thin film coated at 500°C were performed to examine the surface morphology of TiO_2 thin films in detail. The analyses showed that the thin films were coated homogeneously. As shown in Figure 6(b), cracks occur towards the edges of the thin film and these cracks are attributed to the fact that these cracks are caused by thermal stress (Hanabusa et al., 2004).

Through the use of EDS measurements, we investigated the elemental distribution within TiO_2 thin films. The results of our analysis revealed a consistent and homogeneous spread of elements across the films. Figure 7 visually represents the corresponding values derived from these measurements. Upon closer examination, it becomes evident that both Ti and O atoms exhibit a uniform distribution throughout the thin films. Notably, the composition is found to consist of 71.8% O and 28.6% Ti by weight

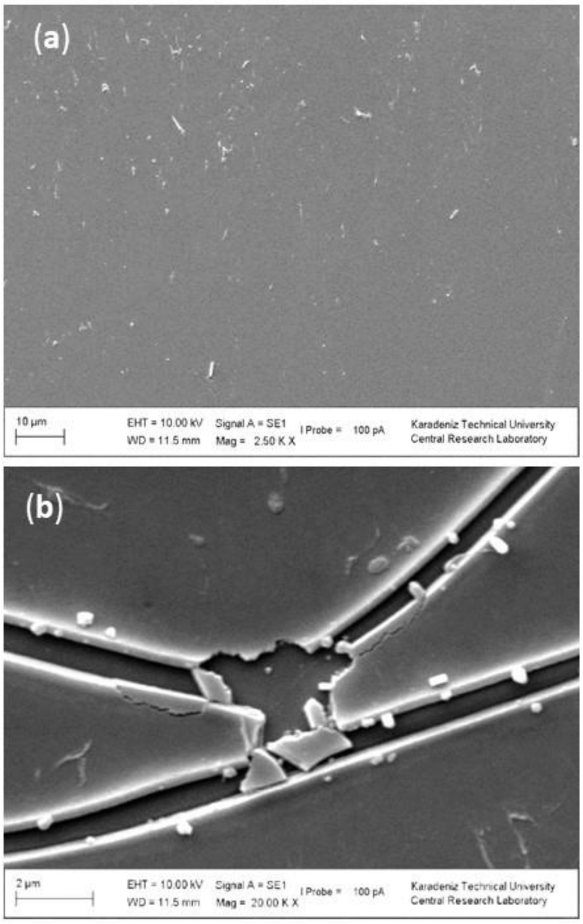

Figure 6. Scanning Electron Microscopy (SEM) images of TiO_2 thin films surface (a) and edge region (b)

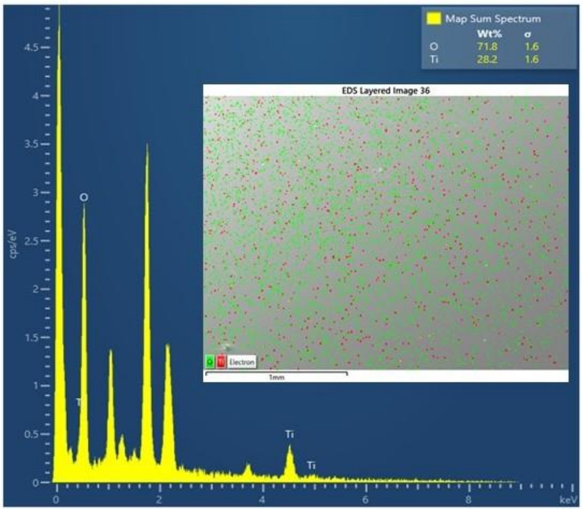

Figure 7. Energy Dispersion Spectroscopy (EDS) patterns of TiO_2 thin film

This specific ratio aligns with the expected composition of the TiO_2 compound. In essence, the data supports the conclusion that TiO_2 thin films exhibit a well-mixed and homogeneous distribution of Ti and O atoms. However, it was observed that the oxygen content was above the expected value. This is thought to be due to the glass substrate used due to the very low thickness of the thin film. However, the XRD and optical measurement results show that stoichiometry is approximately achieved.

4. Conclusions

The aim of this study was to investigate the impact of thermal annealing at different temperatures on the properties of TiO_2 thin films deposited on Quartz glass using the sol-gel method. Various characterization techniques, including XRD, SEM, EDS, and optical measurements, were used to analyze the crystal structure, morphology, elemental composition, and optical properties of the thin films. The optical measurements revealed that annealing at 500°C resulted in the highest transmittance values, indicating improved crystal structure and molecular ordering. The decrease in transmittance at higher annealing temperatures suggested the induction of crystal degradation or structural defects, leading to increased absorbance. The band-gap values calculated using the Tauc method demonstrated a consistent decrease with increasing annealing temperature, indicating a significant change in the electronic properties of the TiO_2 thin films. Also, SEM analysis revealed a homogeneous coating of thin films at 500°C, although thermal stress-induced cracks were observed at the edges. EDS measurements demonstrated a uniform distribution of Ti and O atoms, with a composition consistent with the expected TiO_2 compound. Overall, the results highlight the sensitivity of TiO_2 thin film properties to thermal annealing temperatures and provide valuable insights for optimizing their performance in various optoelectronic and photocatalytic applications, including solar cells, sensors, and photocatalysis. The presented results contribute to the ongoing research in materials science and emphasize the importance of understanding the thermal transformations of crystal structures for tailoring the properties of TiO_2 thin films.

Author Contributions

Kanmaz, İ: Conceptualization, Formal Analysis, Investigation, Methodology, Project Administration, Resources, Supervision, Validation, Visualization, Roles/Writing-Original Draft; Writing–Review and Editing. *Tomakin, M:* Supervision, Conceptualization, Validation, Visualization, Investigation, Resources. *Aytemiz, G*: Investigation, Resources. *Manır, M*: Investigation, Resources. *Nevruzoğlu, V*: Conceptualization, Validation, Investigation, Resources.

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Conflict of Interest Statement

The authors declare that they have no conflict of interest.

Ethical Standards

No Ethics Committee Approval is required for this study.

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