Ellipsometric and ultrasonic studies of nano titanium dioxide specimens doped with Erbium

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Abstract
Nano Er-doped TiO2 thin films prepared by sol-gel technique at different doping concentrations (5%, 7%, 9%, and 11%). The prepared thin films were studied through ultrasonic and ellipsometric measurements. Mechanical properties are known from the ultrasonic method that investigated the effect of the Er-doped amount on the cross-link density, bond strength, elastic properties, and stress-strain relation between atoms of TiO2 thin films. Ellipsometric measurements studied the variation of optical transmittance, energy band gap, refractive index, Urbach energy roughness, and porosity with changing Er-doped amount. Finally, contact angle measurements are done to ensure the self-cleaning property of the prepared thin films. Results deduced that Er-doped enhanced greatly TiO2 thin films, to be used in many industrial applications as self-cleaning glass fabrication.

1. Introduction

Thin films of oxide materials doped with rare earth elements have great interest from researches and industrial applications. Highly oriented and transparent TiO2 thin films used in pigment, solar cells, sensors, self-cleaning glass, smart windows, and water-splitting technology. TiO2 thin films had a wide energy bandgap of 3.2 eV, high thermal stability, high refractive index, good photocatalytic properties, and efficient transmittance in the visible and near-infrared wavelength region [1, 2].

Doping is the introduction of traces of one or more elements to vary thin film properties. Researches proved that doping of TiO2 with a transition metal, rare earth, and noble metal ion had greatly influence [3].

Generally, the rare earth Erbium metal is from the lanthanide family, when it alloyed with Vanadium, decreased the hardness, and increased the workability. Besides, Erbium is mostly used in lasers and optical fibers. Therefore, Erbium is considered a challenging element for doping TiO2 thin films, because scientific researchers seek to improve the various properties of thin films, such as their mechanical, optical, and electrical properties.

The sol-gel method is a fast and low-cost method; therefore, is regarded as the most used technique to prepare TiO2 doped thin films.

Ultrasonic is a reliable method to investigate the mechanical properties of materials. Through ultrasonic velocities, elastic moduli calculated. Also, the ultrasonic study can offer good information about the material structure, by knowing cross-link density, interatomic stress-strain, micro-hardness, etc. Therefore, ultrasonic is a good tool to study thin films.

By optical measurements, many important factors are known; like refractive index, porosity, energy band gap, roughness, thickness, etc. Thus, the optical properties of thin films are widely studied.

Spectroscopic ellipsometer is a non-destructive, non-contact optical technique, which used for the characterization of a thin film sample. By using a fitting modeling approach to the measured ellipsometric parameters, many physical factors; as refractive index, thin-film thickness, transmittance, porosity, energy band gap, Urbach energy can be determined. Thus, the optical properties of thin films are widely studied [4].

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Ultrasonic and ellipsometric studies were used to evaluate the effect of Er doping on TiO2 thin films. The work aimed to prove that the prepared doped films are hydrophobic, so they can be used as a self-cleaning glass.

2. Materials and methods

2.1. Er-doped TiO2 thin films preparation

Pure (TiO2) and Erbium-doped TiO2 (TiO2: Er3+ films were prepared through the sol-gel method and then deposited on microscopic glass slides. The sources of titanium and Erbium were Titanium (IV) isopropoxide (Ti(OC3H7)4 and (Er(NO3)3·5H2O) respectively. Isopropanol and Acetic acid added as solvent and catalyst, respectively. Titanium (IV) isopropoxide with Isopropanol and Acetic acid dissolved in ethanol in a flask (flask A) and stirred for 2 h at 60 °C. Erbium nitrate pentahydrate dissolved in Isopropanol and Acetic acid in a flask (flask B), which was also stirred for 15 min at room temperature. Solution A added to solution B, and the final solution was stirred for 1 h at 60 °C. The obtained final transparent solution used for coating was aged for 24 h at room temperature. The concentration of Er for doping was taken (5%, 7%, 9%, and 11%). The substrate acted as the host surface on which the thin film was deposited. It was a small slide of glass (2 × 1 × 0.1 cm²). Before pouring the film, the substrate surface cleaned well using an ultrasonic cleaner with acetone, ethanol, and distilled water. The sol deposited onto glass using (Spin Coater KW4A) at a rotation speed of 3000 rpm for a period of 30 s. Finally, the deposited films dried in air at 120 °C for 10 min and then annealed at 400 °C in the air at a heating rate of 5 °C min⁻¹ and cooled down to room temperature.

2.2. Ultrasonic method

An ultrasonic pulse-echo technique was used to study the prepared specimens. The ultrasonic equipment consists of a flaw detector (Krautkramer, USIP 20) to display the echoes that are transmitted and received from ultrasonic transducers. In this study, we used two transducers, one for the longitudinal waves (Karl Deutsch, S 12 HB2) and the other for the shear waves (Karl Deutsch, MB2y). The time traveled by the echoes was displayed by the oscilloscope (hp, 4191a Rf).

The prepared thin film specimens had nano thickness, therefore, to overcome the measurements in the blind area (near field) of the transducer, a delay was designed. Firstly, the transducers near field (NF) calculated, to determine the shape of the delay line piece, table 1. The thickness of the delay line must be equal or bigger than the near field of the transducers.

\[
NF = \left(\frac{D_{eff}}{f_0}\right)^2 \frac{1}{4C}
\]

Where \(D_{eff}\) is the effective transducer diameter, \(f_0\) is the operating frequency of the used transducer and \(C\) is the specimen ultrasonic velocity (\(C_l\) is the longitudinal sound velocity in the specimen, \(C_l\) is about 4312.5 m s⁻¹ and \(C_s\) is the shear sound velocity in the specimen, \(C_s\) is about 2816.3 m s⁻¹).

From table 1, the near field of normal and shear used transducers were 17 and 25 mm respectively, i.e. the delay line thickness should be equal or a little bit greater than these values. Therefore, the delay was cubed glass pieces (17 × 17 × 17 mm³ and 25 × 25 × 25 mm³).

2.3. Ellipsometric method

Spectroscopic Ellipsometer PHE-103 Angstrom is an optical and analytical technique that measures the change in the polarization state of the light reflected from the surface of a material.

The specimen measured at the UV/VIS range from 250–900 nm and at an angle of incidence 70°. The light beam is incident on a sample through a polarizer and the reflected beam from the material surface changes the polarization state of the incident beam. After reflection, the beam passes through a quarter-wave plate and another polarizer (analyzer) and then to the detector. The change in the polarization state, which is represented as an amplitude ratio, and the phase difference \(\Delta\), is measured. The fundamental equation of ellipsometer is [5]

\[
\rho = \tan \psi e^{i\Delta}
\]

Where \(\rho\) is the complex reflectance ratio.

After the measurement, data fitting analysis is performed using an optical model (depends on mathematical models) to calculate, and \(\psi\). Fitting analysis is modified until the best match obtained between the data from the
fitting model and the experiment [6]. Physical factors of the specimen such as optical constants, film thickness, roughness, doping concentration, transmittance, and absorption coefficient can be determined [7]. Other optical parameters such as energy gap, Urbach energy, porosity, relative density calculated from those factors [8].

3. Results and discussion

3.1. Thin films thickness
Firstly, the thickness of TiO$_2$ thin film specimens undoped and doped with Erbium are determined by ellipsometric analysis of the experimental data with the fitting models and values between 690 nm and 756 nm obtained as shown in figure 1 [9].

From figure 1, the increment of thickness values with increasing the Erbium dopant is due to the introduction of impurities and defects to TiO$_2$ thin film [13 and 20]. This ensures the growth rate enhancement of the prepared film by Er doping content [10, 11].

3.2. Ultrasonic velocity
The ultrasonic velocity calculated following the below formula:

\[
C = \frac{2x}{t}
\]

Where: \(C\) is the ultrasonic velocity, \(x\) is the thickness of the specimen and \(t\) is the time traveled by the echoes.

From figure 2, it is clear that the ultrasonic velocity decreased as per Er doping content, this referred to the good fitting of Er atoms between the TiO$_2$ thin films’ network. Therefore, the interatomic gaps decreased and the waves’ passage became faster leading to a decrease in the ultrasonic velocity.

3.3. Poisson’s ratio (\(v\))
Poisson’s ratio (\(v\)) is affected by the changes in the cross-link density of the molecular chain network. It is known from a simple formula as follow:

\[
v = \frac{1}{2} \left[ \frac{1}{C_L} - \frac{1}{2} \left( \frac{C_S}{C_L} \right)^2 \right]
\]

\(C_L\) is the longitudinal sound velocity in the specimen, and \(C_S\) is the shear sound velocity in the specimen.

There was a slight increment in the Poisson’s ratio, figure 3, this may be due to the rising in Er content affect the cross-link density of the molecular network in the prepared thin films.

3.4. Elastic moduli
The elastic moduli (longitudinal \(L\), shear \(G\), bulk \(K\), and Young’s \(E\)) reflect the elastic properties of a given material. They can offer information about the material’s rigidity, intermolecular bond forces, etc. Rigid objects such as an iron nail have strong intermolecular forces and rigid lattice patterns, thus they have low elastic
moduli. Not rigid objects such as rubber gloves have a less rigid lattice, their atoms arranged in repeated flexible molecular chains, so they have high elastic moduli.

The elastic moduli of thin films obtained from the following formulas:

\[ E = 2\rho(C_\phi)^2(1 + \nu) \]  
\[ L = \rho(C_\phi)^2 \]  
\[ G = \rho(C_\phi)^2 \]  
\[ K = L - \frac{4}{3}G \]

Where: \( \rho \) is thin-film density (g cm\(^{-3}\)), \( E \) is Young’s modulus, \( L \) is the longitudinal modulus, \( G \) is the shear modulus and \( K \) is the bulk modulus.

The trend of \( G, K, E, \) and \( L \) curves was the decrement with the increment of Er content, figure 4. The undoped TiO\(_2\) thin films (Er 0\%) had the highest elastic moduli values. Er dopant caused the decrement in the films’ elastic moduli. Er dopant caused atoms agglomeration and decreased pores. Also, the intermolecular bond length was shrinkage so the films became more rigid [12, 13].

**Figure 2.** The ultrasonic velocity of TiO\(_2\) thin films as per Er doping percentage.

**Figure 3.** Poisson’s ratio of TiO\(_2\) thin films versus Er doping percentage.
3.5. Micro-hardness
The micro-hardness (H) could characterize the bond strength between atoms in the alloy specimens. It calculated using Young’s modulus (E) and Poisson’s ratio (v) as follow:

\[ H = \frac{(1 - 2v)E}{6(1 + v)} \]

The films’ micro-hardness was raised as per Er doping percentage, figure 5 because the Er dopant led to getting stronger bond strength.

3.6. Lamé constants (\( \mu \) and \( \lambda \))
From the measured ultrasonic velocities, Lamé constants (\( \mu \), \( \lambda \)) can be determined to detect the stress-strain relation between atoms in specimens. They calculated as follow:

\[ \mu = C_L^2 \rho \]  
\[ \lambda = (C_L^2 \rho) - (2\mu) \]

Figure 6 showed the significant decrement of Lamé constants (\( \mu \), \( \lambda \)); this means the interatomic stress-strain in the prepared TiO\(_2\) thin films greatly influenced when the Er dopant increased.
3.7. Ultrasonic attenuation coefficient ($\alpha$)

The ultrasonic attenuation coefficient ($\alpha$) can be used to analyze the material because it easily discovers any variation in the material as a result of any chemical or physical change in the material. It is measured by comparing the amplitudes of the pulses ($u$) that traveled different acoustic paths ($x$) in the specimen under study according to the following equation:

$$\alpha = \left(\frac{1}{(x_2 - x_0)}\right)\ln\left(\frac{u_1}{u_2}\right).$$

The ultrasonic attenuation coefficient expresses the decay rate of echoes in the specimen under test. In figure 7, the attenuation coefficient increased as the Er percentage increased in the prepared TiO$_2$ thin films. Er, percentage increment led to the decrement of intermolecular space so the decay rate of echoes changed causing increment in ultrasonic attenuation coefficient.

3.8. Refractive index ($n$)

The spectral dependence of the refractive index $n$ of TiO$_2$ undoped and doped with Er with different concentrations illustrated in figure 8. The results of the refractive index with different doping concentrations show that the refractive index $n$ increased with increasing the Er concentration on TiO$_2$ thin films.
3.9. Transmittance

The transmittance measurements in the wavelength range 250–900 nm of TiO₂ undoped and doped with Er with different percentages are measured in figure 9.

Figure 9 showed that the transmittance decreased with increasing the percentage of the Er dopant in TiO₂ thin films. The optical transmittance values decreased with increasing Erbium content to thin films, which can be affected by several factors such as scattering of light by surface, surface roughness, refractive index, thickness, and defects introduced to the film [14].

3.10. Roughness

The measurement of surface roughness by ellipsometer is determined by using the fitting algorithm of an effective medium approximation Model (EMA) of 50% material and 50% void. The surface roughness is assumed as a homogeneous layer of optical constants composed of a mix between the optical constants of the two media separating the rough interface. The measured surface roughness is in the range of 0.44 nm and 2.59 nm as in figure 10 [15, 16]. Thus, the Er dopant increased the films’ roughness. The roughness increased with increasing the Erbium dopant concentration, which is due to the introduction of defects or impurities to the band structure of TiO₂ thin film [10, 11, 16].
3.11. Bandgap energy

The Bandgap energy $E_g$ calculated from the Tauc relation, which is as follows [17]:

$$\alpha h\nu = A (h\nu - E_g)^2$$

Where $(h\nu)$ is the photon energy, $h\nu = 1240$/incident wavelength (nm), and $\alpha$ is the absorption coefficient and given by:

$$\alpha = \frac{1}{t} \left[ \ln \left( \left(1 - R\right)^2 / T \right) \right] = 4.\pi. k$/incident wavelength (nm)

Where $R\ , T$ are the reflection and transmission of the light, $t$ is the thickness of thin-film and $k$ is the extinction coefficient of the thin film.

By plotting a relation between $(\alpha h\nu)^{0.5}$ (cm$^{-1}$ eV$^{0.5}$ versus photon energy $(h\nu$, eV), a straight line is obtained as illustrated in figure 11. The values $E_g$ have been estimated from the intercept of these lines with the $x$-axis [10].

Figure 11 clarified that the bandgap decreased with increasing the dopant of Er to TiO$_2$ thin films. This was due to Er acted as a good filler that decreased the pores and gaps in the interatomic structure of the prepared films.

3.12. Urbach energy

Urbach energy $E_u$ is known as the Urbach tail and can be detected in the range of UV/VIS spectra. It is the measurement of the structural disorder due to the localized defects between the valence and conduction bands of thin-film material. The spectral dependence of the absorption coefficient $\alpha$ and photon energy $(h\nu)$ is known as Urbach empirical rule [18],

$$\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)$$

Where $\alpha_0$ is a constant and $E_u$ denotes as the energy of the band tail and is called Urbach energy. Taking the logarithm of the above equation, we get [19]:

$$\ln \alpha = \ln \alpha_0 + \left( \frac{h\nu}{E_u} \right)$$

By plotting a relation between $\ln \alpha$ versus photon energy $(h\nu)$, we get a straight line as in figures 12(a)–(e). The Urbach energy can be determined from the slope of this line.

Figure 13 showed the increment of Urbach energy with the increment of Er content in the prepared TiO$_2$ thin films. The higher value of Urbach energy shows low crystallinity, high impurities, a disorder in the nanomaterials, and large numbers of oxygen vacancies [14].

![Figure 10. Surface Roughness measurements of TiO$_2$ thin films undoped and doped with Erbium.](image-url)
3.13. Porosity and relative density

The porosity is the measurement of the void spaces in the material and calculated from the refractive index of the sample using the equation [20, 21]:

\[
\phi = \left[ 1 - \frac{(n_f^2 - 1)}{(n_d^2 - 1)} \right] \times 100
\]  

Where \(n_f\), \(n_d\) are the refractive indices of sample and pore-free anatase TiO\(_2\). The results in figure 14(a). Show that the porosity decreased with the increment of the concentration of Er dopant to TiO\(_2\) thin films.

From the porosity values, we can determine the relative density of undoped and Er-doped TiO\(_2\) thin films. The relationship between porosity and relative density is reciprocal. As porosity decreases, the relative density increases as illustrated in figure 14(b).

Figure 14(a) clarified the decrement of porosity with the increment of Er doping percentage; Er filled the space between TiO\(_2\) lattices and diminished the pores. In contrast, the relative density of the doped film was direct proportion to Er percentage, figure 14(b).

3.14. Contact angle measurements

The surface tension of the prepared thin films can affect its self-cleaning property. One analytic tool to define this property is the measurement of the contact angle between one drop of liquid (water) and the surface of thin
films. There are two models to measure the contact angle: 1- Wenzel state 2- Cassel-Baxter state. The first one demonstrates the drop of water falling on the solid surface, while the second one deals with the drop of water rolling off on the solid surface to know the ability of self-cleaning. We used smartphones to take photos of the water drops on the thin film surface [22–24]

After measuring the contact angle for all the prepared thin films (pure and doped with Er), we found that the contact angle ($\theta^*$) increased as the percentage of Er increased (from about 93° to about 107°), figure 15.
Figure 13. Urbach energy versus Erbium doping percentage.

Figure 14. (a), (b) shows Porosity and relative density versus Erbium doping percentage.

Figure 15. Contact angle ($\theta^\circ$) variation with Er doping percentage.
Generally, when the contact angle is more than 90°, we can say that the film is hydrophobic. This means the film became more hydrophobic as Er content increased; Besides, it can get rid of dust easily.

4. Conclusion

TiO₂ thin films had greatly influenced by the Er dopant. Er increased thin films’ thickness, ultrasonic attenuation, Poisson’s ratio, micro-hardness, relative density, and refractive index. While Er decreased the ultrasonic velocities, the elastic moduli, Lamé constants, and transmittance. Er made the atoms were more close together. Thus, the interatomic spacing in films’ network diminished, so the bandgap and porosity of films decreased. Urbach’s energy increment with the addition of Er explained that the films showed low crystallinity. Finally, the study tried to demonstrate that Er could enhance the industrial usage of TiO₂ thin films. We benefit from all previously cited measurements to ensure that Er caused an increment in bond strength and the atoms were more close together. Thus, the films transformed to be hydrophobic. Therefore, the Er dopant gave the very important property to TiO₂ thin films, which can get rid of dust easily and they could be used in self-cleaning glass fabrication.

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