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Optical Properties Of Pure TiO_2 Films inlaid with $SnO_2 : ZnO$

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Abstract

In this work, the optical properties of titanium dioxide thin films (TiO_2) inlaid with tin and zinc(SnO_2 -ZnO) and in different weight ratios (0, 3, 5, 7) % were studied. The thin films were prepared using thermochemical spray technology on glass slides at a temperature of (350°C). The optical results revealed poor optical transmittance of unblemished TiO_2 at the end of the ultraviolet spectrum followed by an increase, more than 47%, in the near-infrared spectrum. The thin TiO_2 films revealed greater transparency with a blue shift in the absorption edge when the splicing increased by (SnO_2 -ZnO) and a decrease in the absorption coefficient with the increase in the foil by (SnO_2 -ZnO)According to the results of the electronic transition of the TiO_2 , thin films have a direct and indirect energy gap, about (2.12eV and 3.2eV) respectively. An increase in both types of energy gap was observed with an increase in the concentration of distortion of (SnO_2 -ZnO) In addition, there was also a significant decrease in the refractive index and inertia index with an increase in the concentration of the ratio of distortion in (SnO_2 -ZnO) Keywords:TiO2,Thin Films, Spray pyrolysis, Energy gap,Structural properties , Optical properties.

1.Introduction

Thin-film technology is one of the important technologies that help in the development of electronic science and engineering of surfaces. Due to the thickness of these membranes and their ease of cutting, they are deposited on other materials for use as substrates, depending on the nature of their study and use such as glass, quartz, silicon, aluminum and other metals [1]. Substrate type Recently, they have been used in the manufacture of ordinary and thermal mirrors, filters, panels sensitive to electromagnetic waves, imaging, solar cells and integrated circuits and contributed to the development of computer construction and aviation technology [2]. Thin-film technology contributed significantly to the study of semiconductor properties and gave a clear idea of many of their physical and chemical properties[3]. The method of thermal chemical spraying (CSP) technique has been adopted by many researchers and in our research. CSP has many characteristics. The main ones are simplicity and low cost of used equipment that can be used in normal weather conditions. In addition, membranes and materials with a high melting point can be prepared by this technology and can produce a homogeneous and good surface in large areas that may not be prepared by other methods [4].Titanium dioxide was used as a base material in our study due to its unique properties. It is an inorganic white solid, thermal stability with a large energy gap of 3.2eV, non-flammable and non-toxic with good semiconductor properties [5]. Commercially, it is an important material that has been used in paint and thin-film coating applications because it has high visual transparency [6]. Titanium dioxide is a very valuable material for optical applications in recent years [7-12]. Many efforts have been directed towards transferring the optical sensitivity of TiO_2 from ultraviolet light to the visible light spectrum for the effective use of solar radiation or artificial visible light [13]. The objectives of this work include studying the structural and optical properties of pure thin TiO_2 titanium dioxide films inlaid with tin and zinc (SnO_2:ZnO) in weight ratios (0, 3, 5, 7). After that, finding the possibility of using the prepared membranes in the wide range of electronic applications

2.The theoretical part

2.1 Transmittance:

The transmittance spectrum (T) for the prepared thin films was calculated using the absorption spectrum based on the following formula:[14]$T = exp^{-2.303\,A}$ … … … . . (1)

T:Transmittance and A: Absorption

2.2 Absorption coefficient:

The absorption coefficient (α) was practically determined by measuring absorbance (A) and permeability (T), as follows:[15]$\alpha = 2.303\frac{A}{t}$ … … … … … … … . (2) A: Absorption and t: Thickness

2.3 Energy gap:

The energy gap was calculated according to the relationship:[15]$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^r$ … … … … … … … … … (3)E_g: The light energy gap (eV), hυ absorbed photon energy (eV) and B:is a constant depending on the nature of the material. r: The exponential coefficient depends on the nature of the transitions, it is equal to $(\frac{1}{2})$ for the allowed direct transmission and $(\frac{3}{2})$ for the non-allowed direct transmission, while it is equal to 3 and 2 for the allowed and unallowed indirect transmission respectively.

2.4 Refractive index:

The refractive index (n) is calculated according to the relationship: [15] $n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$ … … … … … … … … … … … . . (4)

R : Thin film reflection

2.5 Inactivity coefficient:

The inertia coefficient (K) represents the energy absorbed into the membrane. Calculated from the relationship: [15]$K = \lambda\alpha / 4\pi$ . . . . (5) λ : wavelength of the incident photon.

3.Practical part:

Ungrafted TiO_2 membranes with weight ratios of (3, 5 and 7) % mixed oxide of thin films SnO_2 and ZnO (TSZ) according to Table (1) using thermochemical spraying technology on the glass substrate at an ideal temperature of (350°C) and a thickness of 125±5 nm Before the sedimentation process, the glass substrates were cut with dimensions of (2.5cm×2.5cm) followed by cleaning with distilled water and ethanol for 15 minutes to ensure that suspended impurities were finally removed. Washed with ethanol To be ready for precipitation.Table 1: Weight ratios % of thin films(TiO_2) smeared (TSZ)

TSZ concentrations %	System
0	TiO_2
3	TiO_2 (0.97):(SnO_2:ZnO) (0.015+0.015)
5	TiO_2 (0.95):(SnO_2:ZnO) (0.025+0.025)
7	TiO_2 (0.93):(SnO_2:ZnO) (0.035+0.035)

A solution of titanium trichloride ($TiCl_3$) with a concentration of 0.05M was used as a source of TiO_2 depending on the following reaction:[24]$2TiCl_3 + H_2O \rightarrow Ti(OH)_2Cl_2 + TiCl_4$ $Ti(OH)_2Cl_2 \rightarrow\downarrow TiO_2 + \uparrow 2HCl$ Doping solutions were prepared from aqueous tin(II) chloride ($SnCl_2$.$2H_2$ O) and aqueous zinc acetate [Zn $(CH_3COOH)_2$.$2H_2$ O] to obtain SnO_2 and ZnO, respectively. The powders were dissolved in distilled water without any other additives. A visible UV spectrometer with a wavelength of 300 to 900 nm with a double beam was used to study absorption, optical transmittance, absorption index, electron transition, refractive index and inertia index. After completing the process of preparing the substrate and solution, the next step was to deposit the thin films. Glass substrates are placed in the middle of the electric heater, which is controlled by Ni Cr / Ni as a kind of thermocouple. After making sure that the solution is located perpendicular and uniformly to all parts of the substrates, selective factors and conditions were relied upon; temperature is about (350°C±5), spray time (5 seconds), stop time (15 seconds), solution flow rate (2 ml / min), spray distance (29cm ± 3) and air pressure (3 Nt. / m^2).Figure 1: shows the room temperature permeability spectrum calculated by equation (2) within the spectrum range 300 to 900 nm.

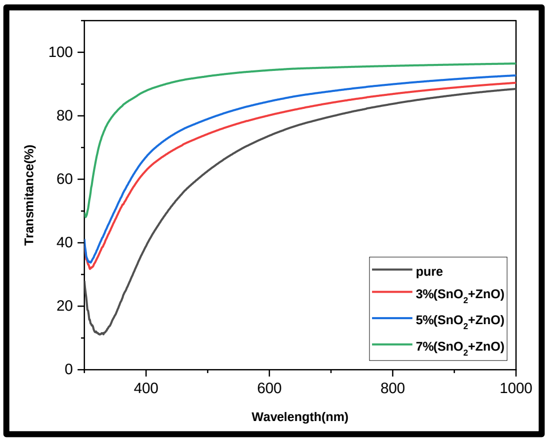


Figure 1: Permeability as a function of the wavelength of untinged and tinged with TSZ (TiO2) The transmittance spectrum mainly consists of two parts. Reveals poor optical transmittance of unblemished TiO_2, less than 20%, at the beginning of the visible spectrum. With slight linear increases in the permeability ratio within the range 325 to 370 nm followed by a jump in transmittance values after the absorption edge to reach the highest value at the end of the spectrum, about 86%, as a result of agreement with [16]. The impaired permeability within this range is due to the high absorption within this region of the spectrum where permeability is inversely proportional to absorption based on equation (1). Figure 1: also shows the clear effect on the permeability spectrum in TSZ steroids with the same behavior for unblemished membranes. It was found that permeability increased with the increase in stimulant concentrations to reach the highest transmittance value, more than 96% at near-membrane infrared at 7% of TSZ. Another observation of the same figure showed that there was a shift in the absorption edges towards short wavelengths (blue offset) with increasing TSZ, as shown in Table 4. This is due to the possession of the description of the nanoparticles of the prepared membranes [17] and the doping process changed the grain size of these nanoparticles [18]. This shift refers to an increase in energy gap values with an increase in TSZ, as shown below.Since the process of distortion has led to a significant increase in transmittance especially in the visible spectrum region, it is possible to utilize membrane types in areas of electronic applications such as optical windows where their effective region is in the visible spectrum range.Table (2) Permeability Results of Pure TiO_2 Films Tinged with Tin and Zinc.

Doping Ratio%	λ_1 (nm)	T %	λ_2 (nm)	T %	λ_3 (nm)	T %
0	٣٢٥	11.08	٥٩4	٥٥.٥5	900	86.52
3	310	31.91	٢٣4	4٥.٦6	900	88.89
5	307	34.18	١٤4	٧٨.٦٩	900	91.54
7	304	48.89	٣٧٦	١٨.٥8	900	96.13

The absorption coefficient is calculated from equation (2) and is shown as a function of the wavelength in Figure (2). All membranes have a strong absorption edge in the ultraviolet region, due to electronic transitions between bands at this wavelength [19]. Figure (2) also shows that the unformed TiO_2 has a strong peak absorption, (18.32×10^{4} cm^{-1}) at a wavelength of 325 nm and then a significant decrease in the absorption coefficient with increasing wavelength. This is due to increased permeability in this spectral band.

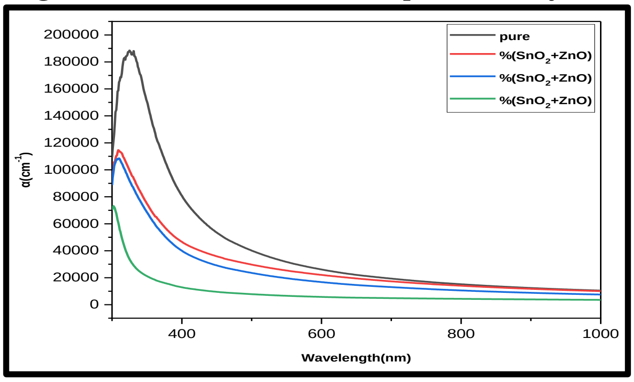


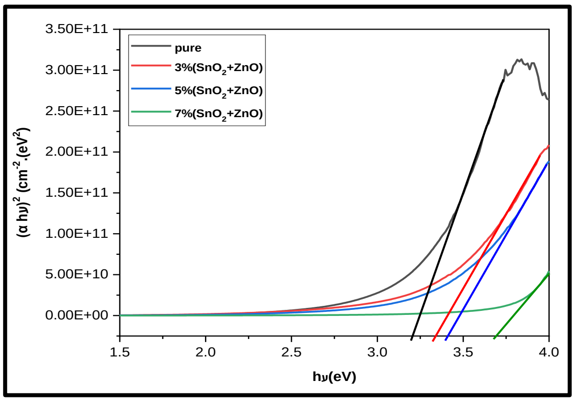
Figure (2) Absorption coefficient variation (α) as a function of the wavelength of pure TiO_2 films inlaid with tin and zincIn general, the absorption coefficient values after distortion with TSZ decreased with the same behavior for unformed membranes, as shown in Table (3). The reason for the low values of the absorption coefficient within the wavelength range from 400 to 900 nm is due to the fact that the electron transition in this wavelength range was minimal. In other words, the energy of the incident photons was not enough to excite these electrons and then transfer them to the valence band of the conduction range [20].Table 3: Variation of absorption coefficient with wavelength: maximum at λ_1, at the absorption edge λ_2, at the end of spectrum λ_3.

Doping Ratio%	λ_1 (nm)	$\alpha \times 10^4$ (cm^{-1})	λ_2 (nm)	$\alpha \times 10^4$ (cm^{-1})	λ_3 (nm)	$\alpha \times 10^4$ (cm^{-1})
0	٣٢٥	18.32	459	4.89	900	1.2
3	310	11.42	423	4.07	900	1.17
5	307	10.73	414	3.59	900	0.88
7	304	7.15	376	1.6	900	0.39

All prepared membranes had an absorption coefficient greater than (10^4 cm^{-1}), which is consistent with [16], giving the impression that the membranes under study would have a direct-type energy gap. According to these results, steroids with this concentration of TSZ can be used in the field of reflective coatings to take advantage of the low absorption property in the spectrum range from visible to infrared.According to several previous studies, titanium dioxide membranes contain both types of energy gap, direct and indirect type. Energy gap values generally depend on many factors, the most important of which is the crystal structure of the thin films of nanoparticles as well as how atoms are distributed and arranged in the crystal lattice [21]. The results of the direct and indirect bandgap calculations are shown in Figures (3 and 4), which were calculated by plotting the relationship between $(\alpha h\upsilon)^2$ as a function of photon energy (hυ) for direct E_g while $(\alpha hv)^{1/2}$ as a function of photon energy (hυ) for indirect E_g depends on equation (3). The direct and indirect light energy gap values represent the point of intersection between the photon energy, the (X) axis, and a straight line extending from the curve $(\alpha h\upsilon)^2$ and $(\alpha hv)^{1/2}$, respectively, at $\alpha = 0$

The direct and indirect optical power gap values are tabulated in Table 4. It is very close to many of the researchers' findings [17,22]. This shows that there is an increase in both types of E_g with an increase in the concentration of impurities may be due to steroids with TSZ resulting in improved crystal growth by reducing localized states and thus reducing structural defects of the crystal structure [23]Table 4: Direct and indirect E_g of untinged and tinged TiO_2 with different concentration of TSZ

Doping Ratio %	*Direct* E_g *(eV)*	*Indirect* E_g *(eV)*
0	3.2	2.12
3	3.3	2.21
5	3.36	2.25
7	3.75	٩١2.



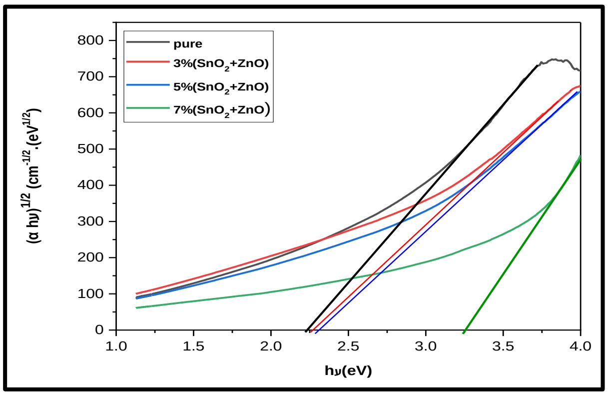


Figure 3: Direct light energy gap change as a function of photon energy

Figure 4: Indirect light energy gap change as a function of photon energy

Figure 4 shows the change in the refractive index of unblemished and tinged TiO_2 with different concentrations of TSZ depending on equation (3). For the unblemished membrane, there is a linear increase in n values within the 340 to 387 nm range and then an exponential decrease to the end of the spectral range at 900 nm. However, the smearing ratios of (3, 5 and 7) % with TSZ indicates a significant reduction in the refractive index and dolve index. This may be the result of a change in the distribution of atoms on the surface of the prepared thin films and then in the roughness of the membranes, and this is consistent with [24], also, it may be due to the decrease in the grain size of the prepared membranes and the surface density of the nanocrystals [8]. Table 5 shows the value of change of the refractive index as a function of the wavelength of all prepared films; the minimum value at λ_1 , at the absorption edge λ_2, and at the end of the spectrum λ_2 for films with high refractive index suitable for anti-reflective coatings and multilayer optical coatings, such as optical fibers, applications [25].Reducing the refractive index with increasing TSZ made the prepared membranes more transparent, which can be used in the field of optical windows [9].

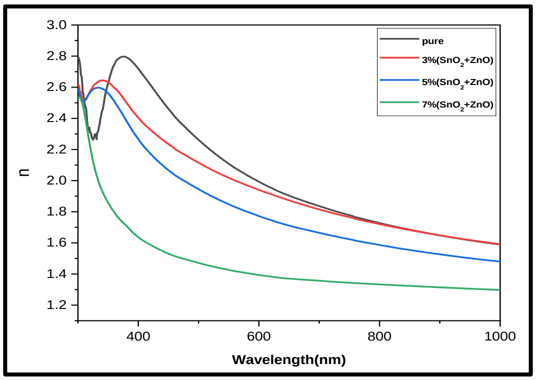


Figure 5: Refractive index variation as a function of wavelength.

Doping Ratio%	λ_1 (nm)	N	λ_2 (nm)	N	λ_3 (nm)	N
0	53٣	2.66	378	2.79	900	1.649
3	327	2.61	340	2.64	900	1.647
5	321	2.56	335	2.59	900	1.526
7	301	2.53	04٣	2.53	900	1.314

Table 5: Change of refractive index with wavelength: maximum n at λ_1 , at the absorption edge λ_2 , at the .end of spectrum λ_3

The dampening coefficient is affected by many factors, including the loss of incident wave energy due to the absorption process. A similar behavior of the absorption coefficient is due to the relationship between them, equation (4). Figure (5) revealed the change in the values of the dormant coefficient with wavelength. The highest dormant coefficient values for the prepared thin films were within the absorption edge followed by a sharp drop to the end of the spectrum, as shown in Table 6. This decrease is due to the amount of radiation that has been diluted on the surface of the membranes [7]. The highest values of the inactivity coefficient within the short wavelength can be attributed to losses in incident radiation energy due to the basic absorption process. In other words, the higher energy of incident radiation means the likelihood of absorption increases. While the low values of the dampening coefficient at long wavelengths can be attributed to the increased permeability within this spectral region of the prepared membranes [26].

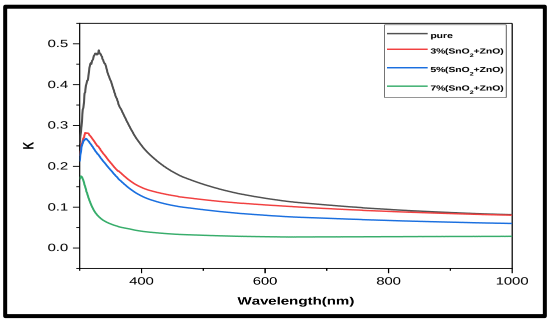


Figure 6: Variation of the inactivity coefficient as a function of wavelength.

Doping Ratio%	λ_1 (nm)	K	λ_2 (nm)	K	λ_3 (nm)	K
0	٣٢٥	0.47	٥٩4	0.17	900	0.085
3	310	0.28	٢٣4	0.13	900	0.084
5	307	0.26	١٤4	0.11	900	0.06
7	304	0.17	٣٧٦	0.04	900	0.028

Table 6: K changes with wavelength: maximum at λ_1 , at the absorption edge λ_2, at the end of the spectrum λ_3.

From Figure (6), it is clear that the unblemished membrane has a rapid decrease in the dolation coefficient within the UV spectrum and then an exponential increase within a visible range followed by relative stability within the infrared spectrum. However, this difference in the behavior of membranes depends on many factors. The initial type of formation, roughness and density of surface membranes, the distribution of atoms, the type of crystal structure, etc. [27]. The effect of the distortion concentration with the TSZ dormant coefficient was reduced by the same absorption coefficient behavior for the same reasons, due to the relationship between α and K, according to relation (5). An important indicator of the low values of the inertia coefficient in the visible and near infrared spectrum range, is that the surfaces of the prepared TiO_2 membranes were smooth [28].

4. **Conclusion**:

Thin films are prepared from unblewed, tinged TiO_2 with different concentrations of SnO_2:ZnO mixture (TSZ) on glass substrates by chemical spray pyrolysis. The results of visual calculations showed an increase in optical transmittance with an increase in the concentration of doping, while the absorption coefficient decreased. The direct and indirect optical power gap increases from 3.2eV to 3.75eV and from 2.12eV to 2.91eV respectively. The TSZ ratio reduced the refractive index from 2.79 to 2.53, while the dormant coefficient has a maximum value within the UV spectrum range.

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