Concentration Effect of Mixed SnO$_2$-ZnO on TiO$_2$ Optical Properties Thin Films prepared by Chemical Spray Pyrolysis Technique

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ABSTRACT

In this work, the concentration effect of mixed tin dioxide and zinc oxide on optical properties of titanium dioxide thin films was studied. Thin films were prepared by using spray chemical pyrolysis technique on glass substrate at 350 °C. The optical results revealed a weak optical transmittance for Un-doped TiO$_2$ at the end of ultraviolet spectrum followed by an increase, more than 48%, at the near IR spectrum. TiO$_2$ thin films revealed more transparent with blue shift in the absorption edge when the SnO$_2$-ZnO mixed increased. A significant decrease in the absorption coefficient with increasing the mixed of SnO$_2$-ZnO. According to the results of the electronic transition of TiO$_2$, thin films have direct and indirect energy gap, about 3.2 eV and 2.11 eV, respectively. An increase in both types of energy gap was observed with the mixing concentrations of SnO$_2$-ZnO increase. In addition, a significant decrease also was in the refractive index and extinction coefficient with the increasing SnO$_2$-ZnO concentration.

1. INTRODUCTION

Thin film technology is one of the important techniques that helps in the development of electronic science and engineering of surfaces. Because of the thinness of these films and the ease of cutting, they are deposited on other materials to be used as substrates, depending on the nature of studying and using such as glass, quartz, silicon, aluminum and other metals [1]. The type of substrate recently, they have been used in the manufacture of ordinary and thermal mirrors, filters and sensitive panels for electromagnetic waves, imaging, solar cells, integrated circuits and they have contributed to the development of building computers and aerospace Technology [2]. Thin film technology contributed significantly to the study of semiconductor properties and it gave a clear idea about many of its physical and chemical properties[3].

The method of chemical spray pyrolysis technique (CSP) has been adopted by many researchers and in our research. CSP has several characteristics; the most important are simplicity and low cost of equipment used which can be used in normal weather conditions. In addition, films and materials with high melting point can be prepared by this technique and they can produce a good homogeneity surface in large areas that may not be prepared in other ways [4].

Titanium dioxide was used as the base material in our study because of its unique characteristics. It is a white inorganic solid, thermal stability with a large energy gap of 3.2 eV, non-flammable and non-toxic with good semiconductor properties [5]. Commercially, It is an important material that has been used in paints and thin films coating applications because it has a high optical transparency [6]. Titanium dioxide constitutes a very valuable material for optical applications in recent years [7-12]. Many efforts have been directed toward transference the optical sensitivity of the TiO$_2$ from UV to the visible-light spectrum for the efficient use of solar radiation or synthetic visible light [13].

The objectives of the present work include studying the doping effect with different concentrations of mixed SnO$_2$-ZnO on the optical properties of titanium dioxide thin films according to the system (TiO$_2$)$_{1-x}$:(SnO$_2$-ZnO)$_x$ with $[(1-x):\frac{x}{2} + \frac{x}{2}]$, where (x= 0, 3, 5, and 7) wt.%. After that, finding the possibility of using the prepared films in the wide fields of electronic applications.

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2. THEORETICAL PART

2.1. Transmittance

The transmittance spectrum (T) of the prepared thin films was calculated using the absorption spectrum depending on the following formula: [14]

\[ T = \exp^{-2.303 A} \]  

(1)

\[ T : \text{Transmittance} \quad \text{and} \quad A : \text{the absorbance}. \]

2.2. Absorption Coefficient

The absorption coefficient (α) was practically determined by the measuring of absorption (A) and transmittance (T), as following: [15]

\[ \alpha = 2.303 \frac{A}{t} \]  

(2)

\[ A: \text{The absorbance after correction, and} \quad t: \text{the thickness.} \]

2.3. Energy Gap

The energy gap was calculated by the following relation: [15]

\[ \alpha h\nu = B(h\nu - E_g)^r \]  

(3)

\[ E_g: \text{Optical energy gap (eV) and } h\nu: \text{absorbed photon energy (eV)} \]

\[ B: \text{Constant depends on the nature of the material.} \]

\[ r: \text{the exponential coefficient depends on the nature of the transitions, it is equal to 1/2 for allowed direct transition and 3/2 for the forbidden direct transition, while it equals to 3 and 2 for allowed and forbidden indirect transition respectively.} \]

2.4. Refractive Index

The refractive index (n) was calculated according to the relation: [15]

\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \]  

(4)

\[ R: \text{thin film reflectance.} \]

2.5. Extinction Coefficient

The extinction coefficient (K) represents the energy absorbed in the film. It was calculated from the relation: [15]

\[ K = \lambda \alpha /4\pi \]  

(5)

\[ \lambda: \text{Incident photon wavelength.} \]

3. EXPERIMENTAL PROCEDURE

Un-doped TiO₂ and doped with (3, 5, and 7) wt.% mixed oxide of SnO₂ and ZnO (TSZ) thin films according to Table1 by using spray pyrolysis technique on glass substrate at optimal temperature of 350°C with 125 nm as a thickness. Before deposition process, the glass substrates were cut with dimensions (2.5×2.5) cm followed by cleaning with D.W and ultrasonically bath for 15 minutes to make sure the removal of oily impurity. Finally, they were washed with D.W to be ready for deposition.

<table>
<thead>
<tr>
<th>System</th>
<th>TSZ concentrations %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TiO₂ (0.97):SnO₂:ZnO (0.015+0.015)</td>
</tr>
<tr>
<td>5</td>
<td>TiO₂ (0.95):SnO₂:ZnO (0.025+0.025)</td>
</tr>
<tr>
<td>7</td>
<td>TiO₂ (0.93):SnO₂:ZnO (0.035+0.035)</td>
</tr>
</tbody>
</table>

Titanium trichloride (TiCl₃) solution with 0.05 M was used as a source of TiO₂ depending on the following reaction: [24]

\[ 2TiCl₃ + H₂O \rightarrow Ti(OH)₂Cl₂ + TiCl₄ \]

\[ Ti(OH)₂Cl₂ \rightarrow \downarrow TiO₂ + \uparrow 2HCl \]

The doping solutions were prepared from Tin (II) chloride dehydrate (SnCl₂.2H₂O) and Zinc acetate dehydrate [Zn(CH₃COOH)₂.H₂O] to obtain SnO₂ and ZnO, respectively. The powders were dissolved in distilled water without any other additives. UV-visible spectrometer with a wavelength ranging from 300 to 900 nm with double beam was used to study the absorption, optical transmittance, absorption coefficient, electronic transition, refractive index and extinction coefficient.

After completing the process of substrate and solutions preparation, thin films deposit was the next step. The glass substrates were placed on the middle of the electric heater, which controlled by NiCr/Ni as a type of thermocouple. After making sure that the solution falls vertically and regularly on all parts of the substrates, a selective factors and conditions were depended; temperature about (350±5 °C), spray time (5sec) , stop time (12sec) , flow rate of solution (2 ml/min), spray distance (29 ± 3cm) and air pressure (3 Nt./m²).

4. RESULTS AND DISCUSSION

Figure.1 shows the transmittance spectrum at room temperature that was calculated by equation (1) within the spectrum range 300 to 900 nm.
The transmittance spectrum is mainly composed of two parts. It reveals a weak optical transmittance for Un-doped TiO$_2$, less than 20%, at the beginning of visible spectrum. Slight linear increases in the percentage of transmittance within the range 325 to 370 nm followed by a jump in transmittance values after the edge of absorption to reach the higher value in the end of spectrum, about 84%, agreement result with [16]. The reason for the weak transmittance within this range was due to the high absorption within this region of the spectrum as the transmittance is inversely proportional to the absorbance based on the equation (1).

Figure 1 also shows the obvious effect on the transmittance spectrum at the TSZ doping with the same behavior for Un-doped films. It was found that the transmittance increased with the increase of the doping concentrations reaching the highest transmittance value, more than 89% at the near IR for the films with 7% TSZ. Another observation of the same figure that showed there was a shift in the edges of the absorption towards the short wavelengths (blue shift) with the increase of TSZ, as shown in Table 2. This is due to the possession of nanoparticle description for the prepared films [17] and the doping process changed the grain size of these nanoparticles [18]. This shift refers to an increase in the energy gap values as TSZ increased, as seen below.

Since the doping process has resulted in a significant increase in transmittance especially in the visible spectrum region, it is possible to benefit from such types of films in the fields of electronic applications as optical windows where its effective region is in the range of the visible spectrum.

**Table 2: Variation of transmittance according to the wavelength: maximum at $\lambda_1$, at the absorption edge $\lambda_2$, at the end of spectrum $\lambda_3$.**

<table>
<thead>
<tr>
<th>Doping Ratio</th>
<th>$\lambda_1$ (nm)</th>
<th>T%</th>
<th>$\lambda_2$ (nm)</th>
<th>T%</th>
<th>$\lambda_3$ (nm)</th>
<th>T%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>327</td>
<td>11.52</td>
<td>387</td>
<td>25.33</td>
<td>900</td>
<td>55.44</td>
</tr>
<tr>
<td>3</td>
<td>324</td>
<td>17.9</td>
<td>370</td>
<td>38.53</td>
<td>900</td>
<td>86.76</td>
</tr>
<tr>
<td>5</td>
<td>317</td>
<td>17.47</td>
<td>362</td>
<td>47.02</td>
<td>900</td>
<td>88.53</td>
</tr>
<tr>
<td>7</td>
<td>314</td>
<td>22.90</td>
<td>358</td>
<td>47.42</td>
<td>900</td>
<td>89.22</td>
</tr>
</tbody>
</table>

The absorption coefficient was calculated from equation (2) and it is shown as a function to the wavelength in Figure 2. All films have a strong absorption edge in the Ultraviolet region, due to the electronic transitions between bands at this wavelength [19]. Figure 2 also shows that Un-doped TiO$_2$ has a strong absorbance peak, $11 \times 10^4$ cm$^{-1}$, at the wavelength of 327 nm then a significant decrease in the absorption coefficient with increasing wavelength. It is attributable to the increase of the transmittance in this spectral range.

**Table 3: Variation of absorption coefficient with wavelength: maximum at $\lambda_1$, at the absorption edge $\lambda_2$, at the end of spectrum $\lambda_3$.**
All prepared films had an absorption coefficient greater than $10^4 \text{cm}^{-1}$, approach to its findings by [16], which gives the impression that the films under study will have an energy gap of the direct type. According to these results, the doping with this concentration of TSZ can be used in the field of reflective coatings to take advantage of the low absorbance property at the spectrum range from visible to infrared radiation.

According to many previous studies, Titanium dioxide films have both types of energy gap, direct and indirect type. The values of the energy gap in general depend on many factors, one of the most important is the crystal structure of the nanoparticle thin films in addition to how the atoms are distributed and arranged in the lattice of the crystal [21]. Results of direct and indirect band gap calculations are shown in the figures 3 and 4, which were calculated by plotting the relation between $(\alpha h\nu)^2$ as a function of the photon energy $(h\nu)$ for direct $E_g$ while $(\alpha h\nu)^{1/2}$ as a function of the photon energy $(h\nu)$ for indirect $E_g$ depends on equation (3). The values of the direct and indirect optical energy gap represent the intersection point between the photon energy, ($X$-axis), and a straight line extending from a curve of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$, respectively, at $\alpha = 0$.

The values of direct and indirect optical energy gap were tabulated in Table 4. They are very close to many results by researchers [17,22]. This shows that there was an increase in both types of $E_g$ with an increase of dopant concentration. That may be due to the doping with TSZ which leads to improve the crystalline growth by reducing localized states and thus reducing the structural defects of the crystal structure [23].

Table 4: Direct and indirect $E_g$ for Un-doped TiO$_2$ and doped with different concentration of TSZ.

<table>
<thead>
<tr>
<th>Doping Ratio</th>
<th>Direct $E_g$ (eV)</th>
<th>In direct $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.2</td>
<td>2.11</td>
</tr>
<tr>
<td>3</td>
<td>3.3</td>
<td>2.42</td>
</tr>
<tr>
<td>5</td>
<td>3.38</td>
<td>2.6</td>
</tr>
<tr>
<td>7</td>
<td>3.47</td>
<td>2.67</td>
</tr>
</tbody>
</table>

Figure 5 shows the variation of refractive index for Undoped TiO$_2$ and doped with different concentrations of TSZ depending on equation (4). For Un-doped film, there is a linear increase in $n$ values within the range 340 to 387 nm then exponential decrease to the end of the spectral range at 900 nm. However, doping with 3, 5 and 7% with TSZ refers to a significant decrease in refractive index and extinction coefficient. That may be as a result of changing in the atoms distribution on the surface of the prepared thin films and then in the roughness of films, this is in agreement with [24], also, the reason may be due to a decrease in the granular size of the prepared membranes and the surface density of the nanocrystals [8]. Table 5 shows the variation value of refractive index as a function to the wavelength for all prepared films; minimum value at $\lambda_1$, at the absorption edge $\lambda_2$ and at the end of spectrum $\lambda_3$. Films with high refractive index are suitable for anti-reflective coatings and multilayer optical coatings, such as optical fibers, applications [25].
Decreasing the refractive index with TSZ increase made the prepared films more transparent, which could be used in the field of optical windows [9].

![Graph](image_url)

Fig. 5: The variation of refractive index as a function for the wavelength.

Table 5: Variation of refractive index with wavelength: maximum n at $\lambda_1$, at the absorption edge $\lambda_2$, at the end of spectrum $\lambda_3$.

<table>
<thead>
<tr>
<th>Doping Ratio%</th>
<th>$\lambda_1$ (nm)</th>
<th>n</th>
<th>$\lambda_2$ (nm)</th>
<th>n</th>
<th>$\lambda_3$ (nm)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>643</td>
<td>2.66</td>
<td>387</td>
<td>2.65</td>
<td>900</td>
<td>2.38</td>
</tr>
<tr>
<td>3</td>
<td>365</td>
<td>2.65</td>
<td>370</td>
<td>2.64</td>
<td>900</td>
<td>1.60</td>
</tr>
<tr>
<td>5</td>
<td>347</td>
<td>2.64</td>
<td>362</td>
<td>2.58</td>
<td>900</td>
<td>1.57</td>
</tr>
<tr>
<td>7</td>
<td>337</td>
<td>2.64</td>
<td>358</td>
<td>2.57</td>
<td>900</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The extinction coefficient is influenced by many factors, including the loss of incident wave energy due to the absorption process. A similar behavior to the absorption coefficient is due to the relationship between them, equation (5). Figure 5 revealed the changing in the extinction coefficient values with the wavelength.

![Graph](image_url)

Fig.6: The variation of extinction coefficient as a function for the wavelength.

Table 6: Variation of K with wavelength: maximum at $\lambda_1$, at the absorption edge $\lambda_2$, at the end of spectrum $\lambda_3$.

<table>
<thead>
<tr>
<th>Doping Ratio%</th>
<th>$\lambda_1$ (nm)</th>
<th>K</th>
<th>$\lambda_2$ (nm)</th>
<th>K</th>
<th>$\lambda_3$ (nm)</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>327</td>
<td>0.231</td>
<td>387</td>
<td>0.17</td>
<td>900</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>324</td>
<td>0.188</td>
<td>370</td>
<td>0.11</td>
<td>900</td>
<td>0.045</td>
</tr>
<tr>
<td>5</td>
<td>317</td>
<td>0.184</td>
<td>362</td>
<td>0.105</td>
<td>900</td>
<td>0.041</td>
</tr>
<tr>
<td>7</td>
<td>314</td>
<td>0.156</td>
<td>358</td>
<td>0.101</td>
<td>900</td>
<td>0.038</td>
</tr>
</tbody>
</table>

From Figure 6, it is clear that Un-doped film has a rapid decrease in the extinction coefficient within the UV spectrum and then an exponential increase within a visible rang followed by relatively stability within infrared spectrum. However, this variation in the behavior of films depends on many factors; elemental type of the composition, roughness and density of the surface films, atoms distribution, the type of the crystalline structure, etc. [27]. The TSZ dopant concentration effect was decreased the extinction coefficient with the same behavior of absorption coefficient as the same reasons, because of the relation between $\alpha$ and K, according to relation (5). An important indicator from the low values of the extinction coefficient in the visible and near IR spectrum range, that the surfaces of the prepared TiO2 films were smooth [28].

5. CONCLUSION

Thin films of Un-doped TiO2 and doped with different concentrations of SnO2-ZnO mixture (TSZ) on glass substrates are prepared by chemical spray pyrolysis. Results of optical calculations showed an increase in optical transmittance with increase of the dopant concentration, while the absorption coefficient decreases. Direct and indirect optical band gap increases from 3.2 to 3.47 eV and from 2.11 to 2.67 eV, respectively. The TSZ doping ratio reduced refractive index from 2.65 to 2.57, while the extinction
coefficient has the maximum value within the range of UV spectrum.

REFERENCES


تأثير تركيز خليط خليط TiO2-SnO2-ZnO على الخصائص البصرية لأغشية الرقيقة TiO2 الكيميائي الحراري

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الخلاصة:
في هذا العمل، تم دراسة تأثير تركيز ثاني أكسيد القصدير وأكسيد الزنك على الخصائص البصرية للأغشية الرقيقة لثاني أكسيد التيتانيوم. تم تحضير الأغشية الرقيقة TiO2 باستخدام تقنية الرش الكيميائي الحراري على قواعد من الزجاج عند درجة حرارة 350 درجة سيلزية. كشفت النتائج البصرية عن نفاذية بصرية ضعيفة لأغشية TiO2 في نهاية الطيف فوق البنفسجي تليها زيادة، أكثر من 48٪، ضمن طيف الأشعة تحت الحمراء القريبة. أظهرت أغشية TiO2 شفافية أعلى وزحف في حافة الامتصاص باتجاه الاطوال الموجية القصيرة مع زيادة نسبة مزيج SnO2-ZnO. انخفاض كبير في معامل الامتصاص مع زيادة تركيز SnO2-ZnO وSnO2-ZnO. وفقاً للنتائج الانتقال الإلكتروني لـ TiO2، تحتوي الأغشية الرقيقة على فجوة طاقة مباشرة وغير مباشرة، حوالي 3.2 فولت و2.11 فولت على التوالي. كانت هناك زيادة في كلا نوعي فجوة الطاقة مع زيادة تركيز خليط TiO2-SnO2-ZnO. إضافة لذلك، هناك انخفاض كبير في معامل الانتشار ومعامل الخسارة مع زيادة تركيز خليط SnO2-ZnO-SnO2-ZnO.

الكلمات المفتاحية: TiO2، أشعة رقيقة، فجوة الطاقة، الخصائص البصرية