Effect Adding PVA Polymer on Structural and Optical Properties of TiO$_2$ Thin Films

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Abstract

Thin films of titanium dioxide TiO$_2$ pure and TiO$_2$:PVA polymer were prepared using chemical spray pyrolysis technique on glass substrate preheated at (350 °C) for TiO$_2$ pure, and at (160 °C) for TiO$_2$:PVA. with spray rate 3sec./1min, and thickness (250nm). The investigation of (XRD) indicates that structural of TiO$_2$ pure and TiO$_2$: PVA thin films they are polycrystalline and XRD investigation is anatase titanium dioxide, intensity of $<101>$ is more than the intensity of $<000>$, $<200>$ and $<105>$ for TiO$_2$ and TiO$_2$:PVA thin films. The optical properties measurement explain the effect of adding PVA on Transmittance, absorptance, refractive index, absorption coefficient and electronic transitions of prepared thin films. and their results observed that filling of PVA caused increase in optical properties generally.

Keywords: titanium dioxide TiO$_2$, chemical spray pyrolysis, PVA, optical and structural properties, thin films.

Introduction

Recently conjugated polymers (cps) and inorganic compounds have been intensively investigated for the applications devices as light emitting diodes, photodiodes, sensor smart microelectronic and photovoltaic (cells) [1,2,3]. TiO$_2$ have the outstanding proportion of high refractive index (N2.5), excellent transmittance in visible as well as high electrical and chemical stability. It has been studied extensively for using in optoelectronic device [4,5] TiO$_2$ was used as electron accepting material because of its non-toxic and abundance availability to indentify physical and structural properties of semiconductor material, the scope of thin films has enabled this opportunity to study semiconductors through the preparation of films [6], because of easily breaking the thin film which is does not exceed only microns thick it is deposited on certain substrate ,such as glass, silicon, and alumina[7]. TiO$_2$ is found naturally as white material, in three forms of crystalline, Rutile (tetragonal), Anatase (tetragonal), and Brokite (orthorhombic)[8], TiO$_2$ films can be prepared by different techniques, such as thermal evaporation in vacuum deposition (TEVD), chemical vapor deposition (CVD), pulse laser deposition (PLD) chemical spray pyrolysis deposition (CSPD) and other method[9,10,11]. Polyvinyl Alcohol (PVA) is a white and granular, it is soluble in hot water but insoluble in cold water and common organic solvents for many applications[12], this polymer chose in this research because of its relative ability for preheating (comparing with other polymers) to deposited on glass. Polyvinyl Alcohol is prepared in water solutions on evaporation of water, transparent films are formed which have high tensile strength and tear resistance[6], PVA polymer has a melting point of 180°C[13] and it has a molecular weights (26,300, 72,000 and 30,000) g/mol[14]. The aim of this research is study adding PVA polymer on some structural and optical properties of TiO$_2$ thin films which prepared by chemical spray pyrolysis technique.

Experimental Work

TiO$_2$ were prepared by chemical spray pyrolysis technique, which spraying an aqueous solution of titanium chloride TiCl$_3$, which prepared with (0.1 ml/ mol) by dissolving in distilled water (50 ml) of (H$_2$O), then the resulting solution was sprayed on clean preheated glass substrate at (350°C). TiO$_2$ thin films were formed according to equation[15].
$2\text{TiCl}_3 + \text{H}_2\text{O} \rightarrow \text{Ti(OH)}_2 \text{Cl}_2 + \text{TiCl}_4$

$\text{Ti(OH)}_2 \text{Cl}_2 \rightarrow \downarrow \text{TiO}_2 + \uparrow 2\text{HCl}$ .......................... (1)

The resulting films were transparent, white yellowish colour, stable free from pen holes and have good adhesive property. Measured by two methods weight and micro balance. The selected thickness were (250 nm).

![Fig.1](image1.png)

*Fig. (1) Equipments of chemical spray pyrolysis system.*

To prepare titanium dioxide doped polymer (poly vinyl alcohol) is added (0.065 g) of PVA to the distilled water and they solve exposure solution to heat with constant stirring and after confirmation of soluble polymer is added to the solution titanium chlorides TiCl$_3$ record advance and then sprayed on the slides glass and degree temperature 160 $^\circ$C producing TiO$_2$:PVA with same thickness (250 nm).

Results and Discussions

A. XRD analysis: The crystalline structure for TiO$_2$ and TiO$_2$: PVA can be recognized by studying the phase of (XRD) for that material, when a beam of (XRD) from mono wavelength incident on film surface, will exhibit peaks on limit angels for each material because of reflecting of Bragg on parallel crystalline surface. XRD instrument is from type (Shimadzu 6000) made in Japan, with the following specifications are Target is CuK$_\alpha$, Wavelength is 1.5406 A, Current is 30 (mA.) and Voltage is (40 KV.). The XRD find that structural of TiO$_2$ thin film it is polycrystalline and XRD investigation is anatase titanium dioxide, intensity of $<101>$ is more than the intensity of $<200>$ and $<105>$ which agrees with (ASTM) card, for TiO$_2$ and TiO$_2$:PVA, as shown in Fig.(2).

![Fig.2](image2.png)

*Fig. (2) XRD pattern of TiO$_2$ pure and TiO$_2$:PVA thin films.*

Lattice constancies (a) and (c) can calculate from the following equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$ ................................. (2)

XRD pattern is observed characteristics diffraction peaks corresponding to the $<101>$, $<004>$, $<200>$ and $<105>$ The values which measured by XRD instrument of diffraction angle (20), interplaner spacing (d) and Full Width at Half Maximum (FWHM) are shown in Table (1) which it emerged adding PVA polymer enhanced the structural properties of TiO$_2$ thin films that means the degree of crystalline increases because the molecules of TiO$_2$ come close together.
Table (1)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>hkl</th>
<th>$A_0$</th>
<th>$D_{ave}$</th>
<th>$FWHM(\beta)$</th>
<th>$2\theta$</th>
<th>$hkl$</th>
<th>$A_0$</th>
<th>$t$</th>
<th>$c$</th>
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</thead>
<tbody>
<tr>
<td>TiO$_2$ pure</td>
<td>101</td>
<td>3.52125</td>
<td>25.2721</td>
<td>0.9233</td>
<td>9.5107</td>
<td>37.8065</td>
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<td>1.5723</td>
<td>3.7906</td>
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<td>004</td>
<td>2.37769</td>
<td>37.8065</td>
<td>47.8792</td>
<td>0.7000</td>
<td>0.5917</td>
<td>0.7000</td>
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<tr>
<td>200</td>
<td>1.89835</td>
<td>25.4502</td>
<td>36.2081</td>
<td>0.1636</td>
<td>0.1962</td>
<td>0.1083</td>
<td>0.1150</td>
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<td></td>
</tr>
<tr>
<td>205</td>
<td>1.87732</td>
<td>48.4497</td>
<td>1.89835</td>
<td>1.87732</td>
<td>1.1897</td>
<td>1.0100</td>
<td></td>
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<tr>
<td>004</td>
<td>2.47889</td>
<td>36.2081</td>
<td>48.4497</td>
<td>0.1083</td>
<td>0.1962</td>
<td>0.1083</td>
<td>0.1150</td>
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<td>105</td>
<td>1.69990</td>
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<td>0.1150</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

B. Optical properties

(1) Transmittance and Absortance

The transmittance and absorptance of prepared films were measured using (UV-1650PC Shimadzu software 1700 1650, UV-Visible recording Spectrophotometer), Japanese company in the wavelength range (300-850 nm), it is found the transmittance decreasing with add polymer that behavior is vice versa with absorpance behavior as in Fig.(3), which means the PVA polymer enhancement the TiO$_2$ thin films absorptance, this attributed that when adding PVA to TiO$_2$ solutions these molecules fills the vacancies between polymer chains.

![Fig.(3) Transmittance and absorptance of TiO$_2$ pure, TiO$_2$:PVA thin films.](image)

(2) Absorption coefficient ($\alpha$)

The absorption coefficient ($\alpha$) of thin films prepared was calculated in the fundamental absorption region from the relation $[7]$:

$$\alpha = 2.303 \frac{A}{t}$$

Where: $A$ : absorptance of the thin film.

$t$ : thickness of thin film, which is 250 nm.

Fig.(4) shows the relation of absorption coefficient as a function of incident photon energy for TiO$_2$ thin films. The figure shows the high variation. Also we can evidently see that TiO$_2$ thin films have high value of absorption coefficient ($\alpha > 10^4$ cm$^{-1}$) which leads to increasing the probability of occurrence direct transitions. From the same figure we can notice an increasing in absorption coefficient when we add PVA. This is due to the formation of localized levels near the edge of connection, that means this decreasing could be attributed to the changes in the particle size distribution function of formed thin films.

![Fig.(4) Absorption coefficient of TiO$_2$ pure, TiO$_2$:PVA thin films.](image)

(3) Refractive index (n)

The refractive index (n) of the prepared thin films was calculated according to the following equation $[10]$.

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

Where: $R$: reflectance of thin film.

Fig.(5) shows the variation of refractive index (n) with photon energy of the prepared thin films. The increase may be attributed to higher packing density and the changes in the particle size distribution function of TiO$_2$ structural, this the enhancement of growth crystalline this attributed to the molecules of TiO$_2$ come close together when add PVA polymer$[3,6]$.
Refractive Index of TiO$_2$ pure, TiO$_2$:PVA thin films.

(4) Energy gap ($E_g$)

All electronic transitions for the prepared thin films were studied, the direct allowed energy gap in the fundamental absorption region of TiO$_2$ thin films was calculated from relation: \cite{16}

$$\alpha h\nu = B (h\nu - E_g)^r$$ .................................................(5)

Where:

$h\nu$: photon energy.
$E_g$: direct allowed energy photon.
$B$: constant depends on the type of transition.
$r$: exponential constant, its value depended on type of transition,
$r=1/2$ for the allowed direct transition,
$r=3/2$ for the forbidden direct transition.

Fig.(6-a) shows the relation of $(\alpha h\nu)^2$ against photon energy, from straight line obtained at high photon energy the direct allowed energy gap could be determined which was equal (3.195eV) at thickness (250nm), and Fig.(6-b) shows direct forbidden energy gap equal (3.052eV). The increase may be attributed to the improvement of growth crystalline that leads to crystallinity of anatase phase\cite{17}.

<table>
<thead>
<tr>
<th>Optical Constants</th>
<th>TiO$_2$ pure</th>
<th>TiO$_2$:PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>T%</td>
<td>84.29</td>
<td>67.95</td>
</tr>
<tr>
<td>A%</td>
<td>9.02</td>
<td>16.7811</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>73100 cm$^{-1}$</td>
<td>78658.69 cm$^{-1}$</td>
</tr>
<tr>
<td>$n_0$</td>
<td>2.57</td>
<td>2.64</td>
</tr>
<tr>
<td>Allowed Energy Gap $E_g$</td>
<td>3.352eV</td>
<td>3.195 eV</td>
</tr>
<tr>
<td>Forbidden Energy Gap $E_g$</td>
<td>2.383 eV</td>
<td>2.011 eV</td>
</tr>
</tbody>
</table>
Conclusions

The following major conclusions be drawn from this work on the doped dependence on optical properties and the crystalline structure for TiO\(_2\) and TiO\(_2\):PVA prepared thin films:

1. XRD pattern is observed characteristics diffraction peaks which measured by XRD instrument of diffraction angle (2\(\theta\)), interplaner spacing (d) and Full Width at Half Maximum (FWHM), PVA enhances the general structural properties of TiO\(_2\) thin films that means PVA increased tie-up of bonds between Ti and O atoms which means the molecules of TiO\(_2\) come close together.

2. Prepared thin films have high values of absorption coefficient for the wavelength range (300-850 nm), It is increased when add PVA polymer.

3. Absorption and refractive index of TiO\(_2\) thin films increase as film doped with PVA.

4. The direct allowed energy gap of TiO\(_2\) and TiO\(_2\):PVA thin films was (3.195–3.052 eV) respectively, and forbidden energy gap was (2.109–2.383 eV) for TiO\(_2\) and TiO\(_2\):PVA thin films respectively. This means the PVA decreased the energy gap of TiO\(_2\).

From enhancements for structural results, absorption and electronic transitions for optical properties of TiO\(_2\) thin films prepared, can be using it as benefactor of solar cells after adding PVA polymer.

References


الخلاصة