Effects of Mn doping on the characterization of nanostructured TiO$_2$ thin films deposited via chemical spray pyrolysis method

Esraa H Hadi$^{1}$, Mustafa A Abbsa$^{2}$, Abdulhussain A Khadayeir$^{3}$, Ziad M Abood$^{1}$, Nadir F Habubi$^{1}$, Sami S Chiad$^{1}$

$^{1}$Department of Physics, College of Education, Mustansiriyah University, Baghdad, Iraq.
$^{2}$Department of Physics College of Education, University of Al-Qadisiyah, Al-Qadisiyah, Iraq.

$^{*}$Corresponding Author. E-mail: dr.sami@uomustansiriyah.edu.iq.

Abstract

Nanostructured TiO$_2$:Mn thin films at diverse concentrations of Mn were deposited via chemical spray pyrolysis method (CPM). The XRD patterns hexagonal wurtzite structure with a dominant peak towards (101) plane. The Grain size of the deposited films is about (10.71-12.71) nm with Mn, whereas the strain (%) parameter decrease from 32.34 to 27.26 with Mn. AFM images show the TiO$_2$:Mn effects surface morphology of the film, The grain size was in the area of (91.13), (67.79) and (64.94) nm for the (TiO$_2$, TiO$_2$:2% Mn, TiO$_2$:4% Mn) respectively. Surface roughness of TiO$_2$ Thin films are RSM 16.6 to 3.68 nm, The average transmittance of the samples was 75 to 85% in the visible wavelength range from 300 to 900 nm. The bandgap values were 3.35 eV (undoped) to 3.15 eV (4 % Mn).

Keywords: TiO$_2$, thin films, XRD, UV-Vis, Transmittance, gap energy.

1-Introduction

TiO$_2$ is a transparent oxide, processes wide bandgap falls in the area of 3.0 - 3.4 eV [1-4]. Besides, TiO$_2$ is non-toxic, chemical stability, high optical transmittance and a refractive index, between 2.4 - 2.9 [5-10]. TiO$_2$ is employed in many optical devices, biomedical applications, dye sensitised solar cells, [5, 6, 11]. TiO$_2$ can be amorphous or crystalline (anatase and rutile)[12]. Anatase is recognized as an superb photocatalytic activity [12], but rutile form, has stability at high temperatures, and refractive index [13]. Amorphous form of TiO$_2$ was utilized in variety of biomedical applications [14].

Many methods were employing for the deposition of TiO$_2$ films, such as sol-gel method [15-16], chemical vapor deposition [17], chemical spray pyrolysis [18, 19] sputtering [20], pulsed laser deposition [21, 22, 23].

In this work studied TiO$_2$ thin film was deposited via chemical spray pyrolysis method. This technique is known to be suitable for preparing thin films with controlled structure, composition.

2-Materials and Methods
TiO$_2$ and Mn-doped TiO$_2$ films were prepared on optical glass substrates via CSP method. The aqueous solution containing 0.05 M of Titanium acetate (Ti(CH$_3$COO)$_2$·2H$_2$O) and 100 mL of deionized water was used to obtain the matrix solution. To prepare the doping material 0.1M of Mn nitrate trihydrate (Mn(NO$_3$)$_2$·3H$_2$O) to dissolve in deionized water of dopant as a volumetric percentage 2 and 4%. Substrate temperature preserved at 450°C during deposition process. Nitrogen was used as a carrier gas, space among substrate and nozzle was preserved at 30 cm. spraying time, spraying rate and the time interval between two spray processes was 9 S, 5 mL/min and 2 min respectively, Film thickness was obtained by Gravimetric technique and was nearly 300 ± 30 nm. XRD was utilized to obtain film structure, while the AFM was employed to obtain film topography. Transmittance was obtained via UV/Vis/NIR spectrophotometer.

3-Result and discussion

Figure 1 displays XRD patterns of the deposited films. TiO$_2$ thin film (thickness 300 nm) is 25.33°, 30.80°, 48.01°, and 64.10° correspond to anatase (101), (121), (231) and (133) planes, respectively. Strong peak at (101) was noticed, which agrees with ICDD card no 29-1360.

To understand the crystalline TiO$_2$ particles, the grain size $D$ of TiO$_2$ films was predestined from the $\beta$ (FWHM) of (101) diffraction peak using the Scherrer formula [24,25, 26]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

(1)

Where $\lambda$ is the x-ray wavelength, $\theta$ is the Bragg diffraction angle, $\beta$ is the full width at half maximum (FWHM) of the peak. It can be seen from Table 1 that $\beta$ decreases when TiO$_2$ concentration increases up to TiO$_2$: 4% Mn, the grain size of TiO$_2$ particle is about (10.71 - 12.71) nm, with Mn concentration as listed in Table 1.

The dislocation density ($\delta$) and lattice strain ($\varepsilon$) were predestined via the following equations [27, 28, 29]:

$$\delta = \frac{1}{D^2}$$

(2)

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

(3)

We found that $\varepsilon$ of TiO$_2$ films is about (32.34 - 27.26), which refers to low defects. The calculated structural parameters are offered in Table 1.

Figure (2) represents each of the FWHM, $D$, $\delta$ and $\varepsilon$ versus doping.
Figure 1. XRD-patterns crystalline size of the prepared films.

Table 1. Grain size, optical band gap and structural parameters of the prepared films.

| Samples          | (hkl) Plane | 2θ (°) | FWHM (°) | Grain size (nm) | Optical bandgap (eV) | Dislocations density (× 10^{14} lines/m²) | Strain (× 10^{-4}) |
|------------------|-------------|--------|----------|-----------------|----------------------|------------------------------------------|-------------------|
| TiO_2 pure       | 101         | 25.33  | 0.76     | 10.71           | 3.35                 | 87.18                                    | 32.34             |
| TiO_2: 2% Mn     | 101         | 25.01  | 0.70     | 11.62           | 3.25                 | 74.06                                    | 29.81             |
| TiO_2: 4% Mn     | 101         | 24.88  | 0.64     | 12.71           | 3.15                 | 61.90                                    | 27.26             |
Figure 2. FWHM (a) Grain size (b) Dislocation (c) Strain (d) of the prepared films.

Figure 3 displays the AFM images of the deposited films at different Mn content. It was seen that the films show good quality and pyramidal shape distributed over entire surface. This increase in pyramidal shape proved that crystallinity and surface roughness was enhanced with increase in doping content. The grain size of the deposited films was in the range of (91.13), (67.79) and (69.94) nm for the (TiO$_2$ pure, TiO$_2$: 2% Mn and TiO$_2$: 4% Mn) respectively. The root mean square (RMS) values was seen to be decrease from 18.6 to 3.68 nm with doping and average surface roughness $R_a$ values was seen to decrease from (16.6-3.19) nm. There was an enhance in $R_a$, which assures the use of these films in solar cells and photodetectors [30].

AFM parameters versus dopant concentration were given in Figure 3 (a$_3$, b$_3$, and c$_3$) respectively. Table (2) represent the values of AFM parameters.
Figure 3. AFM images of the prepared films (a1, b1 and c1), granularly distributed (a2, b2 and c2) and variation of AFM parameters via doping (a3, b3 and c3).

Table 2. AFM parameters of the deposited films.

| Samples        | Average Particle size (nm) | Roughness Average (nm) | R. M. S. (nm) |
|----------------|----------------------------|------------------------|--------------|
| TiO2 pure      | 91.13                      | 16.6                   | 18.6         |
| TiO2: 2% Mn    | 67.79                      | 11.3                   | 13.3         |
| TiO2: 4% Mn    | 64.94                      | 3.19                   | 3.68         |

Figure 4 offers transmittance spectra of deposited thin film. The transmittance (400-800 nm) show a decrement with the increment of Mn content. The absorption edge red shifted with the increment of Mn content, thereby increasing absorbing radiation [31].

The direct energy gap $E_g$ of the deposited thin films was evaluated by plotting $(a\nu)^2$ versus $(\hbar\nu)$ figure 5. utilizing Tauc formula [32, 33, 34]:

$$\frac{a\nu}{\hbar
\nu} = A \left(\frac{\hbar\nu - E_g}{\hbar}\right)$$

Where $\hbar \nu$ is the photon energy, and $\alpha$ is the absorption coefficient, which expressed as [35, 36, 37]:

$$A \left(\frac{\hbar\nu - E_g}{\hbar}\right)$$
\[ \alpha = \ln\left(\frac{1}{T d}\right) \]  

(5)

Where \( d \) is film thickness. Figure 6. shows the absorption coefficient is of the order of \( 10^4 \) cm\(^{-1}\). The bandgap increased with the increase of Mn concentration. The value of bandgap was in the area of 3.35 eV - 3.15 eV for the deposited films. The bandgap values are shown in Table 1, which indicate the decrease in bandgap via doping.

Figure 4. Transmittance for the prepared films.
Figure 5 \((a\hbar\nu)^2\) Vs \(h\nu\) of the prepared thin films.

Figure 6 \(\alpha\) Vs \(h\nu\) of the prepared thin films.
4-Conclusions
Anatase TiO$_2$ films were successfully deposited via CPM. The films exhibit hexagonal wurtzite crystal structure with a dominant peak toward (101) plane. The grain size of deposited TiO$_2$ films was about (10.71-12.71) nm, whereas the strain (%) parameter decreased from 32.34 to 27.26 nm with Mn. Surface topography of the deposits films via atomic force microscope (AFM) indicates that grain size was observed in the range of (91.13), (67.79) and (64.94) nm with Mn content respectively.

The average transmittance of the samples are 75 to 85% in the visible wavelength range from 400 to 700 nm while the value of bandgap of deposited film is about 3.35 eV - 3.15 eV.

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