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Abstract

Nanostructured TiO\textsubscript{2} was prepared utilizing spray pyrolysis deposition (SPD). The characterization of the deposited films was studied with Bi dopant. The XRD analysis indicate that films are polycrystalline with a preferred orientation along (110) direction. AFM shows a porous morphology structure. The optical properties were obtained by UV–visible spectrophotometer, which show that these films are highly transparent above 85% in visible region with a slightly influenced upon Bi content. The energy gap was shifted from 3.1 to 2.6 eV, versus doping.

Keywords: Bi:TiO\textsubscript{2}, SPD, Optical, structure, topographical.

Introduction

Titanium oxide (TiO\textsubscript{2}) is a n-type semiconductor with wide energy bandgap of 3.2. TiO\textsubscript{2} show pleasant properties like transparency to visible light, high refractive index and a low absorption coefficient. [1, 3]. TiO\textsubscript{2} has three main crystalline structures: anatase (tetragonal), brookite (orthorhombic) and rutile (tetragonal). Rutile is commonly stable at high temperatures [4]. The phase conversion from anatase to rutile relys on film growth process, which might be influenced by defect concentration, grain boundary concentration, and particle packing [5, 6]. It is found that the optical properties and electronic structure of TiO\textsubscript{2} is modified under the doping of transition elements. These transition metals minimize the rate
of recombination of hole-electron pairs, and improve the “interfacial charge transfer efficiency”[7,8]. There are several TiO$_2$ thin film deposition techniques including sol–gel deposition [9], spray pyrolysis [10], pulsed laser deposition [11], e-beam evaporation [12], chemical vapor deposition [13], and reactive magnetron sputtering [14]. In this paper pure Titanium dioxide and doping with Bismuth 2% and 4% thin films prepared in the simple and low cost of CSP in order to study their optical, structural and Morphology.

**Experimental**

Titanium dioxide (TiO$_2$) and Bismuth (Bi) -doped TiO$_2$ thin films were prepared by 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 cupric nitrate trihydrate (Bi(NO$_3$)$_2$·3H$_2$O) to dissolve in deionized water of dopant as a volumetric percentage 2 and 4., which kept constant during the deposition process for TiO$_2$ and Bi doped TiO$_2$. Substrate temperature was kept at 450$^\circ$C during deposition process. Nitrogen was used as a carrier gas, distance between substrate and nozzle was kept at 29 cm. spraying time, spraying rate and the time interval between two spray process were 8 S, 5m L/min and 1 min respectively.

Film thickness was obtained by Gravimetric technique and was about 350±30 nm. Transmittance and Absorbance spectra were recorded via Shimadzu double beam spectrophotometer. Structural parameters were analyzed by X-ray diffractometer (Shimadzu, model: XRD-6000, Japan) using CuK$\alpha$ radiation. AFM (AA 3000 Scanning Probe Microscope) was utilized to study deposited thin films surface.

**Results and Discussion**

XRD patterns of pure and Bi doped TiO$_2$ thin films are displayed in Fig. 1. The films exhibit polycrystalline tetragonal crystal structure. The diffraction peaks observed in XRD patterns of all the films corresponds to (110), (200), (201) and (203) planes of the typical tetragonal crystal structure of TiO$_2$ thin films compared with JCPDS card no 00-021-1236. The diffraction peaks were indexed to srilankite planes and Bi relative peaks were not observed implying that Bi was doped into TiO$_2$ lattice. At doping of Bi the intensity of (110) plane increases which may be due to increase in the mobility of titanium and oxygen atoms which led to the
increase in the nucleation of crystallization phase of srilankite TiO$_2$. The crystallite size ($D$) of the sample was calculated from full width at half maximum (FWHM) $\beta$ of the (110) peak of anatase TiO$_2$ by Debye Scherrer equation [15, 16].

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

Where $\lambda$ (1.54060 Å) is x-ray wavelength. The Dislocation density ($\delta$) was calculated by using relation [17]:

$$\delta = \frac{1}{D^2} \left( \frac{\text{lines}}{m^2} \right)$$

The micro strains ($\varepsilon$) were caused by crystalline defects and determined using the following relation 3 [17, 18]:

$$\varepsilon = \frac{\beta \cos \theta}{4} \left( \frac{\text{lines}^{-2} \cdot m^{-1}}{} \right)$$

The variation of $D$ and lattice parameters with dopant Bi was calculated and the findings are recorded in Table 1, which assures that $D$ full in the category of nano. The Crystallite size of the plane (110) increase with increase concentration doping in Bi. The improving in the crystallinity of the films are confirms decreasing in defects. This also confirms from the grain size, which is increased by increasing the concentration doping in Bi.

**Table 1:** Structural data of TiO$_2$ with different Bi doping by (SPD).

<table>
<thead>
<tr>
<th>Bi (%) Doping</th>
<th>(hkl) Plane</th>
<th>2$\Theta$ (Deg.)</th>
<th>Lattice constant (Å)</th>
<th>FWHM (Deg.)</th>
<th>D (nm)</th>
<th>((\varepsilon)) (Line$^2$m$^{-1}$) $\times 10^4$</th>
<th>((\delta)) (Line. m$^{-2}$) $\times 10^{15}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(110)</td>
<td>24.93</td>
<td>a b c</td>
<td>0.88</td>
<td>9.17</td>
<td>38.64</td>
<td>11.883</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.45 9.18 5.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>(110)</td>
<td>24.93</td>
<td>a b c</td>
<td>0.86</td>
<td>9.41</td>
<td>37.64</td>
<td>11.277</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.45 9.18 5.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(110)</td>
<td>24.93</td>
<td>a b c</td>
<td>0.80</td>
<td>10.05</td>
<td>35.24</td>
<td>9.883</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.45 9.18 5.14</td>
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</tr>
</tbody>
</table>
The surface morphologies of pure TiO$_2$ and different concentration Bi doping films are illustrated in Fig. 2. The surface morphology of the pure TiO$_2$ film was composed of different grain size with average diameter 80 nm, average roughness (Ra) 1.07 nm and the root mean square (R. M. S) 1.3 nm. In addition, it was found that the films deposited at 2% and 4% Bi doping were increase slightly in average diameter (97.45-123.47) nm, Ra and R. M. S were getting the same behaviors in addition to that some grain was sharp as shown in Fig. 2 e The increased values of Ra and RMS of the films, indicating its good polycrystalline structure at the surface. The R.M.S and average roughness ($R_a$) of prepared films are shown in Table 2. As can be seen the $R_{rms}$ and $R_a$ follow the dopant.
**Fig.5:** a. AFM image of pure TiO$_2$ thin films. e. and f. AFM images of the doped Bi: TiO$_2$ 2% and 4%.

**Table3:** surface morphology of TiO$_2$ with different Bi doping by (SPD).

<table>
<thead>
<tr>
<th>mn doping (%)</th>
<th>Avg. Diameter (nm)</th>
<th>$R_a$ (nm)</th>
<th>R. M. S. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>92.44</td>
<td>1.07</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>97.45</td>
<td>4.07</td>
<td>4.64</td>
</tr>
<tr>
<td>4</td>
<td>123.47</td>
<td>19.0</td>
<td>22.5</td>
</tr>
</tbody>
</table>
Transmittance spectra of the films are obtained by UV-Vis. spectrophotometer in the wavelength range between 200 to 900 nm Fig. 3. It is clear that when the concentration doping increases then transmittance slightly decreases. All films show high transmittance above 80% in the visible region. Since the calculated energy band gaps of pure films are approximately 3.1 eV. Therefore, these films absorbs photons with wavelength less than 400 nm, according to the relation \( \lambda \text{ (nm)} = \frac{1240}{E_g \text{ (eV)}} \). All these films show high absorption in the wavelength below than 600nm. When the wavelength of light increased from 550 nm, then its transmittance increases. Up to 600nm, the maximum obtained transmittance is 80%. Therefore, these films can be used for the protection of optoelectronic devices from UV radiations.

The absorption coefficient (\( \alpha \)) for each wavelength was calculated from equation 4 [19]

\[
\alpha = 2.303(A/T)
\]

Fig. 4 shows absorbance spectra of the deposited samples. It was clear that absorbance increased via increase Bi content, and that all the films have values of absorption coefficient (\( \alpha >10^4 \text{ cm}^{-1} \)) this means that the direct transition is possible occurs. Bi dopant altered local lattice symmetry and defect, which could modulate absorbance and material properties [20].

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**Figure3.** Transmittance with wavelength of pure and 2\% and 4\%Bi: TiO\(_2\) thin films.
Fig. 4. Absorption coefficient with wavelength in respectively of pure and 2% and 4% Bi:TiO$_2$ thin films.

The optical energy bandgap of pure TiO$_2$ and doped Bi thin films are calculated by the following Tauc’s relation [21, 22].

\[(a\nu) = A(\nu - E_g)^n\]

Where \(n\) equal to \(\frac{1}{2}\) or for direct transition. \(A\) is a constant quantity, \(E_g\) is the bandgap energy, \(h\nu\) is photon energy. Optical bandgap energy is determined by plotted a graph between \(\nu\) and \(a\nu\) is explained in Fig. 5. The calculated band gap energy for pure TiO$_2$ and doped of Bi 2% and 4% thin films are 3.1, 2.8 and 2.6 eV, respectively. This decrease bandgap is due to the increase in doping of the films which is according to the literature [23].
Figure 5. Indirect bandgaps of pure and 2% and 4% Bi: TiO$_2$ thin films.

**Conclusions**

The structure, optical properties, and surface morphology of nanostructure TiO$_2$ and different Bi dopant concentrations films deposited by CSP were investigated. XRD results display polycrystalline structure. All films show high transmittance above 85% in the visible region. Bandgap decreases with increase in doping of films. The films deposited at 2% and 4% Bi doping were increase slightly in average diameter (97.45-123.47) nm. The Ra and R. M. S follow the average diameter.

**Acknowledgments**

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References


