Effect of Al Doping on Thickness, Optical, Morphological and Structural Properties of TiO\textsubscript{2} Thin Film Prepared by Spin Coating Method


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1. Introduction

Titanium dioxide (TiO\textsubscript{2}) thin film is a most popular semiconducting material. When it is doped with metallic dopants is properties changes. TiO\textsubscript{2} has also application in pigments and photo-catalytic activity [1]. The novel properties of TiO\textsubscript{2} were published in 1970 [2]. Since then various types of research works are carried out. Because of the electron transport properties of TiO\textsubscript{2}, optical and electrical properties are varies and it works very efficiently [3, 4]. There exist various route of preparing TiO\textsubscript{2} and its thin film [5]. Fujishima and Honda first determined the photo-catalytic properties of TiO\textsubscript{2} in 1972 [6]. Now-a-days the properties can be changed by using various types of dopants like Al. DSSC solar cell was developed by O’Regan and Graetzel and influenced by the properties of oxide compound [7].

The properties of the thin films depend on its fabrication method. Sol-gel, sputtering, spin coating, dip coating etc. methods have been used to prepare TiO\textsubscript{2} film [8]. Spin coating method is a low cost method for thin film preparation [9]. In this work, spin coating method was used to prepare thin films. The films were deposited on normal seedless glass slide. The rotation was about 2000 rpm. Optical, and morphological, thickness and structural characterizations were carried out by UV-Vis spectrometer, SEM, AFM, and XRD techniques.

2. Experimental Methods

Pure TiO\textsubscript{2} thin film and Al doped TiO\textsubscript{2} thin films were deposited on glass substrates using spin coating method. Titania (TiO\textsubscript{2}, powder) and Al nitrate were used to prepare thin film. Precursors were prepared using TiO\textsubscript{2} solution of 0.5 M and then doped with Al. AI solutions also made in a separate beaker. Then both of the solutions were mixed for preparing thin film forming precursor of different concentration.

The seedless glass slides were cleaned with distilled water, ethanol and ultrasonic bath respectively. Then the films were prepared using homemade spin coater. Each film was prepared from 0.3ml of precursor solution. The size of the glass slide was 15 mm × 15 mm × 1 mm. The slide was spun in air for 60s at 2000 rpm. Finally the prepared films were annealed in a muffle furnace at 15 °C/min heating rate up to 450 °C and soaking time was 30 minutes.

Keywords: Spin Coating, Thin Film, Optical Properties, Surface Roughness.

3. Results and Discussion

3.1 Thickness Measurement

Thickness depends on electrical and optical properties of thin film. The thickness of solid films was measured by Thomson [10]. In thin film experiments, thickness measurement is an important parameter. We used gravimetric analysis for determining thickness of thin film. The thickness of the film can be expressed by Eq. (1):

\[ t = \frac{m}{\rho A} \]

where \( \rho = \) density, \( A = \) area of the film and \( m = \) mass of the film. According to different concentrations of different films, resultant thicknesses are shown in the following Table 1.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Avg. Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M TiO\textsubscript{2}</td>
<td>473</td>
</tr>
<tr>
<td>2% Al doped</td>
<td>473</td>
</tr>
<tr>
<td>4% Al doped</td>
<td>476</td>
</tr>
<tr>
<td>6% Al doped</td>
<td>479</td>
</tr>
</tbody>
</table>

Due to varying concentration thickness varies which is shown in Table 1. With 2% Al doped doesn’t change thickness due to interstitial position of Al. After that concentration the thickness increases. Thickness changes with concentration within a certain limit. Most of the thesis work and research related to thin film shows the optimum thickness for thin film is below 500 nm in some special cases it is about below 1 micrometer. Our resultant films fulfill the standard condition of thickness of thin film.

3.2 Optical Transmittance

Optical transmittance was determined using UV-Vs. single beam spectrophotometer (Halo SB-10). Transmittance was 80% (max) for 0.5 M TiO\textsubscript{2} without dopant. When the doping concentration (Fig. 1) reaches at higher amount 2%, 4% and 6%, the absorbance shows a significant increment in the visible region.
Al dopant increases the absorbance spectrum of TiO$_2$. Metal creates a new energy level as a result the amount of more energy needed to excite an electron, so the absorbance increases. Maximum absorbance is observed by 6% Al doping. The absorbance spectra are shown in Fig. 2.

### 3.3 Band Gap

The absorbance coefficient ($\alpha$) of the undoped thin film and with dopant films was calculated using Eq. (2).

$$\alpha = \frac{1}{t} \ln \frac{1}{T}$$  \hspace{1cm} (2)

where, $t$ is the films thickness calculated (using eqn-1) and $T$ is the transmission of the films. Finally ($\alpha h \nu$)$^2$ was determined from the optical data analysis. The band gap curve is shown in the following Fig. 3.

### 3.4 AFM Analysis

The surface morphology of the film was carried out by using Atomic Force Microscopy (AFM). The surface morphology of undoped TiO$_2$ and the morphology of Al doped thin films are shown in the Fig. 4. With increasing the amount of Al doping the size of the crystal become broader.

### 3.5 XRD Analysis

For determining the crystal structure of thin films XRD was carried out with a radiation source of Cu K$\alpha$ and the wavelength was $\lambda = 1.54 \text{Å}$. The method of Full Width at Half Maxima (FWHM) was used to determine the exact $2\theta$ positions. The grain size of the films was measured by using the Scherrer's formula from XRD patterns [11].

The Fig. 5 shows the X-ray diffraction patterns prepared by spin coating method. The films are spun at 2000 rpm and annealed at 450 °C. All the prepared films are shown anatase phase. Increase in the Al concentration the peak become sharper.

$$D = \frac{0.9 \times \lambda}{B \cos \theta}$$  \hspace{1cm} (3)

The crystal structure of thin film depends on the amount of concentration of dopants. It is found that diffraction peak located at 20=25.258° (A)(101). By using the Eq (3) the grain size was calculated.

The peak of pure TiO$_2$ decreases at 6% it shows a massive change in the pattern than pure TiO$_2$. The calculated grain size is given in Table 3.

<table>
<thead>
<tr>
<th>Amount of Al doping (%)</th>
<th>Surface Roughness, $R_q$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>12.23</td>
</tr>
<tr>
<td>2% Al</td>
<td>41.10</td>
</tr>
<tr>
<td>4% Al</td>
<td>67.35</td>
</tr>
<tr>
<td>6% Al</td>
<td>85.15</td>
</tr>
</tbody>
</table>

### Table 3 Grain sizes of undoped and Al doped thin film

<table>
<thead>
<tr>
<th>Name</th>
<th>Bragg’s Angle (degree)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped TiO$_2$</td>
<td>12.61</td>
<td>13.46</td>
</tr>
<tr>
<td>Al doped (2%)</td>
<td>12.632</td>
<td>19.51</td>
</tr>
<tr>
<td>Al doped (6%)</td>
<td>12.629</td>
<td>26.95</td>
</tr>
</tbody>
</table>
4. Conclusion

Thickness of the film increases within increases concentration up to a certain limit. If we increase the concentration the films become thick. The optical band gap decreases with Al impurities into the thin film. AFM analysis proves there is no crack on the film surface and the roughness increases with dopant. Al doping has a great impact on the grain sizes of the film and the grains become larger due to Al doping compared to undoped thin film.

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References


