Influence of substrate and annealing temperatures on optical properties of RF-sputtered TiO₂ thin films

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TiO₂ thin films were deposited on unheated and heated glass substrates at an elevated sputtering pressure of 3 Pa by radio frequency (RF) reactive magnetron sputtering. TiO₂ films deposited at room temperature were annealed in air for 1 h at various temperatures ranging from 300 to 600 °C. The structural and optical properties of the thin films were investigated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and ultraviolet–visible–near infrared (UV–VIS–NIR) spectrophotometry. XRD results show that as-grown and post-annealed TiO₂ films have anatase crystal structure. Higher substrate and annealing temperatures result in a slight increase of crystallinity. TiO₂ films deposited at different substrate temperatures exhibit high visible transmittance and the transmittance decreases slightly with an increase in annealing temperature. The refractive indices (at λ = 550 nm) of the as-deposited and annealed films are found to be in the range of 2.31–2.37 and 2.31–2.35, respectively. Extinction coefficient decreases slightly with increasing substrate and annealing temperatures. The indirect and direct optical band gap of the as-grown films increases from 3.39 to 3.42 eV and 3.68 to 3.70 eV, respectively, with the increase of substrate temperatures. Annealed TiO₂ films also exhibit an increase in the values of indirect and direct optical band gap.

1. Introduction

Over the last few decades, titanium dioxide (TiO₂) has been widely investigated for its interesting optical, photocatalytic and electronic properties. For its high refractive index, wide band gap and good chemical stability in adverse environment, TiO₂ films are employed for a variety of applications such as in optics industry [1], single or multilayer optical coatings [2–4], dye-sensitized solar cells [5], dielectric applications [6], self cleaning purposes [2] and photocatalytic layers [7]. The highly transparent TiO₂ films have also been widely used as anti-reflection coatings for increasing the visible transmittance in heat mirrors [8]. As a dielectric, TiO₂ is one of the most popular materials for the purpose of anti-reflection coatings [3,4,9,10].

TiO₂ can exist as an amorphous layer and also in three crystalline phases: anatase (tetragonal), brookite (orthorombic) and rutile (tetragonal). Only rutile phase is thermodynamically stable at a higher temperature. The refractive indices at 500 nm for anatase and rutile bulk titania are about 2.5 and 2.7, respectively [11]. There are many deposition methods that can be used to prepare TiO₂ thin films, such as electron-beam evaporation [12], ion-beam assisted deposition [13], DC reactive magnetron sputtering [7], RF reactive magnetron sputtering [5,14], sol–gel methods [15,16], chemical vapor deposition [17] and plasma enhanced chemical vapor deposition [6]. The properties of the titanium oxide films depend not only on the preparation techniques but also on the deposition conditions. Physical vapor deposition (PVD) technology is still a mainstream production tool for functional coatings. Sputter deposition techniques are widely utilized methods to obtain uniform and dense TiO₂ thin films with well-controlled stoichiometry. RF magnetron sputtering is used to deposit TiO₂ films with high refractive index, low absorption and smooth surface in the multilayer optical coating applications. Heat-treatment is one of the utilized ways to obtain better optical properties of TiO₂ films [11,18]. To our knowledge, only few reports are available which explore the influence of sputtering pressure and annealing treatment on the optical properties of RF magnetron sputtered TiO₂ films [11,21].

In this work, RF reactive magnetron sputtering was used to deposit anatase TiO₂ films on heated and unheated glass slides maintaining an elevated sputtering pressure of 3 Pa. The films were also subjected to annealing treatment. The effects of substrate and annealing temperatures on the structural and optical properties of anatase TiO₂ films are presented and discussed in this paper.
2. Experimental

TiO₂ thin films were deposited on microscope glass slides at room temperature, 200 and 300 °C by RF reactive magnetron sputtering of titanium target (purity 99.99% and diameter 100 mm). Prior to each deposition, the titanium target was pre-sputtered in an argon atmosphere in order to remove oxide layers. The sputtering chamber was evacuated down to $5 \times 10^{-4}$ Pa by a turbomolecular pump. The sputter deposition was performed using a mixture of Ar (purity 99.999%) and O₂ (purity 99.999%) at a ratio of 45:10 sccm (standard cubic centimeter per minute) supplied as working and reactive gases, respectively, through independent mass-flow controller. During sputtering, the working pressure and RF power was kept constant at 3 Pa and 250 W, respectively. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally they were rinsed with distilled water and dried by blowing dry nitrogen (purity 99.999%). TiO₂ films deposited at room temperature were annealed at 300, 400, 500 and 600 °C using an electric furnace for 1 h in air.

The phases present in the TiO₂ films were analyzed by an X-ray diffractometer (Model-D5000, Siemens) using Cu Kα radiation ($\lambda = 0.15406$ nm) and operating at an accelerating voltage of 40 kV and an emission current of 40 mA. Data were acquired over the range of 2θ from 20 to 80° at a sampling width of 0.1° and a scanning speed of 1.2 ° min⁻¹. The XRD method was used to study the change of crystalline structure. The surface morphology and microstructure of the as-grown and annealed TiO₂ thin films were also investigated by a field emission scanning electron microscope (FEI Quanta 200 FEG–SEM). The thickness of the as-deposited film was also measured under the SEM.

The optical transmission spectra of TiO₂ thin films were recorded by a double-beam spectrophotometer (Jasco 570) in the range of 250–2500 nm. The measurements were taken at a normal incidence using a reference blank substrate. From the transmission spectra, Swanepoel method [19] was used to calculate the film thickness, optical constants, absorption coefficient and optical band gap of the films.

3. Results and discussion

3.1. Structure

Fig. 1 presents the XRD patterns of as-grown and annealed TiO₂ films. From Fig. 1a, it is found that the TiO₂ thin films deposited at room temperature, 200 and 300 °C are polycrystalline having anatase phase only. The as-grown film at room temperature is found to be crystalline which is in good agreement with earlier studies [20,21]. For a crystalline phase to develop, the depositing atoms should have sufficient energy. This gives the atoms sufficient mobility to position themselves to low energy positions leading to the formation of crystalline phases. High substrate temperatures can achieve the sufficient energy to generate crystalline phases. Although at a high pressure the depositing species have lower energy, there are suggestions that high density negative oxygen ions are movable at high pressure which impart high energy to the growing film [20]. This may be the reason for the growth of crystalline anatase phase in the present study at low temperature and high deposition pressure (3 Pa). On the other hand, TiO₂ films deposited at higher substrate temperatures are found to be crystalline due to higher energy of impinging particles. As the substrate temperature increases, few weak peaks belonging to anatase (0 0 4) and (2 0 4) planes are found to appear. It indicates a slight increase of crystallinity. The diffraction patterns of the as-deposited films at room temperature and annealed at 300, 400, 500 and 600 °C are shown in Fig. 1b. It is observed that the intensity of anatase (1 0 1) peak shows insignificant variation but anatase (2 0 0) peak shows a slight increase in its intensity with increasing annealing temperature. Few weak peaks representing (2 0 4) and (2 2 0) planes are also observed in the films annealed at 500 and 600 °C. The appearance of those new peaks suggests a slight improvement of crystallinity.

The SEM micrographs for surface morphologies of as-grown and annealed TiO₂ films are presented in Fig. 2. In general, the films are found to be flat. Small surface features can only be seen at a very high magnification (100,000×) under the FESEM. The sample grown at room temperature possesses tiny elongated features, about 100 nm in length. Both higher substrate and annealing temperatures tend to make the surface features more nodular. Sun et al. [17] observed an increase in the size of granular features for the TiO₂ films with the increase of annealing temperature up to 600 °C.

3.2. Optical properties of TiO₂ thin films

The optical thickness for the as-deposited film at room temperature is evaluated to be 315 nm using Swanepoel method [19]. The thickness value is in good agreement with the cross-sectional image by SEM shown in Fig. 3. Similarly, the optical thicknesses of the films deposited at 200 and 300 °C are found to be 335 nm and 345 nm, respectively.
The optical spectra of as-deposited TiO$_2$ films are shown in Fig. 4a. It is found that the average transmittance of all as-deposited films is above 75% in the visible region. From Fig. 4a, it is observed that deposition temperature does not affect the transmittance. It may be attributed to the slight variation of crystallinity and the absence of phase transformation in the as-grown anatase TiO$_2$ films. Wang et al. [21] reported higher visible transmittance in their RF-sputtered TiO$_2$ films with anatase phase. They also observed an insignificant variation of transmittance for the samples deposited at various working pressures. In this work, a slight decrease in transmittance is observed with the increase of annealing temperature as shown in Fig. 4b. Among the films, the as-deposited film at room temperature seems to have better transmittance in the visible range. The film annealed at 600 °C have the least transmittance. It may be attributed to the light scattering loss for its higher surface roughness. Saini et al. [22] and Yang et al. [13] also reported the decrease of transmittance with increasing annealing temperature.

The curves of refractive index and extinction coefficient for as-grown TiO$_2$ films are shown in Fig. 5. From Fig. 5a, refractive indices at 550 nm for the films prepared at room temperature, 200 and 300 °C are found to be 2.31, 2.37 and 2.35, respectively. The film deposited at 200 °C shows slightly higher refractive index than that of the film at 300 °C. Yang et al. [13] reported the increase of refractive index with higher substrate temperature. Extinction coefficient is found to decrease slightly with increasing substrate temperature as shown in Fig. 5b.

For the increase of annealing temperature from 300 to 600 °C, refractive index is found to increase from 2.31 to 2.35 as shown in Fig. 6a. It is thus observed that there is only a marginal increase in refractive index with substrate heating as well as annealing. The increase may be attributed to higher packing density within the film and a slight increase in crystallinity. Ye et al. [11] also observed the marginal increase of refractive index in their RF-sputtered annealed films. From Fig. 6b, it is found that the extinction coefficient decreases very slightly as the annealing temperature is increased up to 400 °C. But for the films annealed at 500 and 600 °C, there is a slight increase of extinction coefficient. It is observed that extinction coefficient follows a decreasing trend for
the increase in both substrate and annealing temperature. This finding is in good agreement with that of Hou et al. [18].

To quantify the optical band gap of the films, Tauc model [23] is employed in the high absorbance regions of the transmittance spectra.

$$a = A(h\nu - E_g)^r$$  \hspace{1cm} (1)

where $a$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the optical band gap, $A$ is a constant which does not depend on photon energy and $r$ has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions). In this work, direct and indirect band gap were determined by plotting $(a(h\nu)^{1/2})$ vs. $h\nu$ and $(a(h\nu)^2)$ vs. $h\nu$ curves, respectively, with the extrapolation of the linear region to low energies. From Fig. 7a and b, the indirect and direct optical band gap for the as-grown TiO$_2$ film at room temperature are determined to be about 3.39 and 3.68 eV, respectively. Similarly, optical band gap for the as-grown and annealed films are measured and given in Table 1. From the table, it is observed that indirect optical band gap for the as-grown TiO$_2$ film at room temperature increases from 3.39 to 3.42 eV with the increase of substrate temperature. The direct band gap for the films deposited at room temperature, 200 and 300 °C are found to be 3.68, 3.69 and 3.70 eV, respectively. The indirect band gap for as-deposited films found in this work are in good agreement with the findings of Wang et al. [21], and Karuppasamy and Subrah-
where \( n_p \) is the refractive index of the porous thin films; \( n \) is the refractive index of bulk TiO\(_2\). From Eq. (2), the porosity for the as-grown and annealed TiO\(_2\) films tabulated from the refractive index at 550 nm are shown in Table 2. From the data, it is found that the porosity ratio decreases with the increase of substrate as well as annealing temperature. Similar trend was reported by Ye et al. [11] for their sputtered TiO\(_2\) films.

### Table 1
Variation of indirect and direct optical band gap of TiO\(_2\) films for different substrate and annealing temperatures.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Optical band gap (eV)</th>
<th>Annealing temperature (°C)</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Indirect</td>
<td>Direct</td>
<td>Indirect</td>
</tr>
<tr>
<td>Room temperature</td>
<td>3.39</td>
<td>3.68</td>
<td>300</td>
</tr>
<tr>
<td>200</td>
<td>3.41</td>
<td>3.69</td>
<td>400</td>
</tr>
<tr>
<td>300</td>
<td>3.42</td>
<td>3.70</td>
<td>500</td>
</tr>
<tr>
<td>400</td>
<td>3.43</td>
<td>3.72</td>
<td>600</td>
</tr>
</tbody>
</table>

### Table 2
Variation of refractive index (\( n \)) and porosity (\( P \)) for TiO\(_2\) films deposited and annealed at different temperatures.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>As-deposited films</th>
<th>Annealing temperature (°C)</th>
<th>Annealed films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )</td>
<td>Porosity (%)</td>
<td>( n )</td>
</tr>
<tr>
<td>Room temperature</td>
<td>2.31</td>
<td>19.0</td>
<td>300</td>
</tr>
<tr>
<td>200</td>
<td>2.37</td>
<td>13.7</td>
<td>400</td>
</tr>
<tr>
<td>300</td>
<td>2.35</td>
<td>15.5</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600</td>
</tr>
</tbody>
</table>

4. Conclusion

The anatase titanium oxide films have been produced by RF reactive sputtering technique on unheated and heated glass substrates at an elevated sputtering pressure of 3 Pa. The crystallization is found to increase slightly in both as-grown and annealed TiO\(_2\) films with the increase of substrate and annealing temperature, respectively. All as-grown TiO\(_2\) films exhibit transmittance higher than 75% in the visible region. Annealing treatment causes a slight decrease in visible transmittance. Refractive index at 550 nm ranges from 2.31 to 2.37 for the as-deposited TiO\(_2\) films. The refractive index is also found to increase slightly with increasing annealing temperature. The extinction coefficient decreases slightly as the annealing temperature is increased up to 400 °C. But for the films annealed at 500 and 600 °C, there is a small increase of extinction coefficient. The indirect and direct optical band gap of the films are found in the range of 3.39–3.42 eV and 3.68–3.70 eV, respectively, as the substrate temperature is increased. With the increase of annealing temperature up to 500 °C, the indirect and direct optical band gap increases from 3.39 to 3.42 eV and
3.68 to 3.72 eV, respectively. But the film annealed at 600 °C shows a lower indirect and direct band gap values of 3.40 and 3.68 eV. The porosity is also found to decrease with the increase of substrate as well as annealing temperatures.

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