Influence of substrate temperatures on structural, morphological and optical properties of RF-sputtered anatase TiO$_2$ films
INFLUENCE OF SUBSTRATE TEMPERATURES ON STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF RF–SPUTTERED ANATASE TiO$_2$ FILMS


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1. INTRODUCTION

TiO$_2$ thin films are frequently used for optical coatings due to their high refractive index, wide band gap, and high stability. Today, thin films of TiO$_2$ are employed in many optical devices in the optics industry [1] and in dye-sensitized solar cells [2] because of their remarkable optical properties. The highly transparent TiO$_2$ films can be used as anti-reflection coatings to increase the visible transmittance in heat mirrors [3]. It is known that the TiO$_2$ films have excellent photocatalytic and photoinduced hydrophilic properties for environmental applications, such as air purification, sterilization, antifogging, and self-cleaning [4]. Sun et al. [5] also reported that the TiO$_2$ coated glass, having good antibacterial, disinfectant, antifogging, and self-cleaning properties, could be widely used in building and automotive glasses. Okada et al. [3] reported that the multilayer of TiO$_2$/TiN/TiO$_2$ could be used in energy-conserving glazings as a heat mirror. Soda-lime ordinary glass has been widely used as a substrate due to the intended application of TiO$_2$ films in energy-conserving glazings. TiO$_2$ can exist in an amorphous state as well as in three crystalline phases: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic). The rutile phase is thermodynamically stable at high temperatures. The refractive index at 550 nm of anatase and rutile titania is about 2.5 and 2.7, respectively [6].

Many deposition methods have been used to prepare TiO$_2$ thin films, such as electron-beam evaporation [7,8], ion-beam assisted deposition [9,10], DC reactive magnetron sputtering [11], RF reactive magnetron sputtering [12,13], sol-gel dip coating method [14,15], sol-gel spin coating method [16], chemical vapor deposition [5], and plasma enhanced chemical vapor deposition [17]. High transmittance in the visible region ($\lambda=380-760\text{nm}$), high refractive index, and low absorption are the important optical requirements for heat mirrors. They can be achieved by the optimization of deposition techniques as well as deposition parameters.

For practical applications, deposition parameters have to be optimized to achieve the desired structure and properties in the films. The sputter deposition technique can produce adherent and uniform film over wide areas. The deposit stoichiometry can also be well-controlled. A number of studies on the deposition of TiO$_2$ films by sputtering have appeared in the literature recently [2,6,11,13,18–21]. Different variation of sputtering, such as DC magnetron sputtering [11,19,20], pulsed DC magnetron sputtering [18], RF magnetron sputtering [2,6,13] and pulsed AC magnetron sputtering [21] have been used by researchers. TiO$_2$ films deposited at room temperature and at low pressure (less than 2 Pa) were reported to be amorphous [6,11,18,20]. On the other hand, several reports [2,16,22] found that TiO$_2$ films deposited at higher pressures (2 Pa or above) were polycrystalline with enhanced optical properties. However, to the best of our knowledge, there are few papers concerned with the investigation of the influence of substrate temperatures on the structural, morphological, and optical properties of TiO$_2$ films deposited on soda-lime glass at an elevated sputtering pressure.

In the present study, TiO$_2$ films have been deposited on soda-lime glass substrates by RF magnetron sputtering at a total sputtering pressure of 3 Pa. The effects of substrate temperatures on the structural, morphological, and optical properties of the films have been described.

2. EXPERIMENTAL DETAILS

Anatase TiO$_2$ thin films were prepared on microscope glass slides as substrates by radio-frequency (RF) reactive magnetron sputtering of Ti target of 4 N purity. First, the target was pre-sputtered in an argon atmosphere in order to remove the oxide layer. The sputtering was performed under a mixture of 46 sccm (standard cubic centimeters per minute) of Ar (99.999%) and 10 sccm of O$_2$ (99.999%) atmosphere supplied as working and reactive gases, respectively, through an independent mass-flow controller. The sputtering chamber was evacuated down to $5 \times 10^{-3}$ Pa by the turbomolecular pump and the working pressure was kept at about 3 Pa. During the depositions, the RF power was 250 W and the substrates were kept at room temperature, 200 and 300 °C, respectively using the same deposition time of 16 hours. Prior to deposition, the glass substrates were sequentially cleaned in an ultrasonic bath with acetone and ethanol. Finally, they were rinsed with distilled water and dried.

The crystalline quality of the TiO$_2$ films was investigated by x-ray diffraction (XRD) measurements (Model-D 5000, Siemens) in θ–2θ geometry using Cu K$_\alpha$ radiations ($\lambda=0.15406$ nm). The grain size of the films was calculated by using the Scherrer equation:

$$d = \frac{0.89\lambda}{B \cos \theta}$$
where $d$ is the grain size, $\lambda$ the wavelength of the x-ray, $B$ the full-width at half-maximum of diffraction peak (FWHM), and $\theta$ is the diffraction angle.

The UV-visible-NIR optical transmission spectra of TiO$_2$ thin films were recorded using 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. The Swinney method [23] was used to calculate the optical thickness, refractive index ($n$), and optical band gap ($E_g$) of the films from their transmittance spectra. The thickness of the as-deposited film at room temperature was cross-checked with the SEM cross-sectional image captured using a field emission scanning electron microscope (FEI Quanta 200 FEG-SEM). The depth profiles of the sample deposited at 300°C were analyzed by Auger electron spectroscopy (Jeol-JAMP 9500F field emission scanning Auger microscope, Japan). The Auger spectrum was acquired using 10 keV electron beam acceleration voltage and a beam current of 12 nA. For surface morphology, atomic force microscope (AFM) images were recorded using a Nanoscope IIIa scanning probe microscope controller in a tapping mode.

3. RESULTS AND DISCUSSION

3.1. Structure

A cross-sectional image of the as-deposited TiO$_2$ film on the unheated substrate is shown in Figure 1. It is found that the thickness of the film is approximately 330 nm.

![SEM cross-sectional image of the TiO$_2$ film deposited at room temperature](image)

The cross-sectional view also shows that the film possesses a granular structure. A few voids are also found in the cross section (arrow). It may be mentioned that Enderle et al. [24] obtained a columnar structure in their dc magnetron sputtered TiO$_2$ films at a power of 60 W.

The diffraction patterns of TiO$_2$ films deposited on substrates that were unheated and heated at 200 and 300°C are given in Figure 2. From Figure 2, as-deposited TiO$_2$ film at room temperature is found to be crystalline and possesses anatase structure as it shows few strong peaks of anatase (101), (200), and (211). It has been observed in the literature that a wide variety of structures can be obtained in sputter deposited TiO$_2$ films depending on the deposition conditions. On unheated substrates, amorphous [6,11,12,18], anatase [2,22,25], rutile [26] and a mixture of anatase/brookite [27] were obtained by different researchers. An analysis of the deposition conditions used by different researchers suggests that TiO$_2$ films deposited at room temperature and at low pressure (less than 2 Pa) were found to be amorphous for both DC reactive magnetron sputtering [11,18] and RF reactive magnetron sputtering [6,12]. However, titania films deposited by sputtering at a pressure 2 Pa or more exhibited anatase phase [2,22,25]. For a crystalline phase to develop, the depositing atoms should have sufficient energy. This gives the atoms sufficient mobility to position them 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 imparts high energy to the growing film [18]. This may be the reason for the growth of the crystalline anatase phase in the present study at low temperature and high deposition pressure (3 Pa).
From diffraction patterns, it is also observed that all the films exhibit characteristic peaks corresponding to anatase crystal planes (101), (200) and (211). Some additional weak peaks along the anatase planes (103), (004), (105), (204), and (220) appear for the samples of heated substrates. However, the peak intensities along the anatase planes (101), (200), and (211) decrease significantly with increasing substrate temperatures. It may be inferred that crystallinity is found to decrease with increasing substrate temperatures.

From Figure 3a, it is observed that few strong titanium (Ti) and oxygen (O) peaks appear in the spectrum. A weak peak of silicon is also observed. But there is no distinct Na peak. The depth profiles of the elements, as shown in Figure 3b, show that silicon (Si) and sodium (Na) are present in the film, but content of Na is less than that of Si. Nam et al. [28] investigated sol-gel TiO₂ films on crown glass after annealing at temperatures of 200–500 °C in air for 3.5 hours. They observed the diffusion of Na and Si in their annealed films. From XPS spectra, Tomaszewski et al. [29] also observed the presence of Na and Si in an annealed (at 350 °C for 1 hour) TiO₂ film prepared by DC magnetron sputtering on soda-lime microscope glass slides. Tada and Tanaka [30] investigated sol-gel prepared annealed titanium oxide films on soda-lime glass substrates. They found a higher amount of Na and a small amount of Si in the film annealed at 500 °C for 10 min. In the present work, the diffusion of a larger amount of Si and a lower amount of Na ions in the film prepared on heated substrates may be attributed to the long deposition time of 16 hours. In this work, the deterioration of crystallinity may be attributed to the diffusion of Si and Na ions into TiO₂ films deposited at higher substrate temperatures.

In the present work, the crystallite size was calculated by Scherrer equation using plane (101). TiO₂ films prepared at different substrate temperatures are seen to have a grain size of ~44 nm. Substrate temperature does not seem to have any significant effect on the grain size. This may be due to the slight decrease in crystallinity and probable diffusion of Na⁺ ions into the films at higher substrate temperatures. A number of researchers have reported on the grain size of sputter deposited TiO₂ films [18,24,31,32]. Liu et al. [32] reported that the grain size of DC sputter deposited anatase film increased slightly from 30–37 nm with increasing oxygen partial pressure during deposition. Karuppusamy and Subrahmanyan [18] obtained grain sizes in the range 28–36 nm for pulsed sputter deposited anatase film on quartz substrate. Nam et al. [28] reported that the particle size for fused silica was about
20% smaller than that for glass slides. They observed the particle size for glass slides from 29 to 37 nm as the annealing temperature is increased from 300 to 500°C. Eufinger et al. [24] found that the as-deposited grain size of DC magnetron sputtered anatase film on microscope glass slides increased from 45 to 60 nm as the sputtering power was increased from 60–180 W. They also observed that the grain size decreased from 100 to 45 nm as argon partial pressure was increased from 0.47 to 2.2 Pa. It is observed that the range of grain size of the deposited films on microscope slides obtained in the present study is close to that obtained by Eufinger et al. [24].

3.1.1. Morphology

The surface morphology of all TiO2 films deposited at room temperature, 200 and 300°C, as recorded by AFM images in the tapping mode, is shown in Figure 4.

![Figure 4: AFM images of TiO2 films deposited at different temperatures: (a) Room temperature, (b) 200 °C, and (c) 300 °C](image)

From Figure 4, it is observed that anatase TiO2 films deposited at different temperatures are compact and dense. Moreover, the as-deposited TiO2 films exhibit a nodular morphology. Deposition temperature does not appear to have a significant effect on the morphology of the film. From AFM images, it is observed that the average surface feature size of the films is less than the grain size of 44 nm calculated by the Scherrer equation. However, the Scherrer equation is known to evaluate the upper limit of the grain size. Figure 5 shows the root mean square (rms) surface roughness for the as-grown films. The rms roughness of the as-deposited film at room temperature is found to be 4.75 nm. It is observed in the figure that the roughness increases from 4.7 to 6.3 nm as the deposition temperature is increased. Hou et al. [21] observed a lower rms roughness (2.38 nm) for their AC magnetron sputter as-deposited film having a comparable thickness to the one in the present study. This is thought to be related to the amorphous structure of their as-deposited films. In addition, Karuppasamy and Subrahmanyan [18] reported a higher rms roughness, 5–9 nm for their as-deposited films obtained by pulsed dc magnetron sputtering.

![Figure 5: Root mean square (rms) roughness for as-deposited TiO2 films at different substrate temperatures](image)

3.2. Optical Characterization of TiO2 Thin Films

In this work, the optical thickness was calculated by the Swanepoel method [23] for the as-deposited films at room temperature, 200 and 300 °C and was found to be 315, 335, and 345 nm, respectively. From the optical measurements, it is observed that thickness of the TiO2 films increases insignificantly, indicating a negligible effect