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# Structural and optical investigations of $TiO_2$ films deposited on transparent substrates by sol–gel technique

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ABSTRACT

An inexpensive and effective simple method for the preparation of nano-crystalline titanium oxide (anatase) thin films at room temperature on different transparent substrates is presented. This method is based on the use of peroxo-titanium complex, i.e. titanium isopropoxide as a single initiating organic precursor. Post-annealing treatment is necessary to convert the deposited amorphous film into titanium oxide ($TiO_2$) crystalline (anatase) phase. These films have been characterized for X-ray diffraction (XRD) studies, atomic force microscopic (AFM) studies and optical measurements. The optical constants such as refractive index and extinction coefficient have been estimated by using envelope technique. Also, the energy gap values have been estimated using Tauc's formula for on glass and quartz substrates are found to be 3.35 eV and 3.39 eV, respectively.



## 1. Introduction

Titanium oxide ($TiO_2$) is one of the most extensively studied transition metal oxide. $TiO_2$ possesses excellent properties such as chemical resistance, good mechanical strength, transparency, as well as insulating properties. $TiO_2$ films are widely used in many optical, biomedical, and microelectronic applications because of low cost material with a high refractive index and high dielectric constant [1]. These $TiO_2$ films carried out for the different applications as in opto-electronic devices, sensors, dye-sensitized photo-voltaic cells, electro chromic displays, planner wave guides, photo-catalysts, etc. [2,3]. The preparation of $TiO_2$ thin films has received great attention during the past several decades because of its remarkable optical, photo-catalytical and electronic properties. $TiO_2$ films can be synthesized by various thin film deposition techniques, such as thermal evaporation [4,5], chemical vapor deposition (CVD) [6], metal organic chemical vapor deposition [7], pulsed laser deposition [8] and sol–gel process [9]. Thin films of $TiO_2$ are frequently used for coatings due to their high refractive index, and high stability, and its properties are easily affected by the technological conditions of deposition process such as substrate temperature and oxygen partial pressure as well as by the post-deposition heat treatment [10]. Tain et al. [11] have demonstrated that the quantum confinement effect in $TiO_2$ thin films prepared by electron beam evaporation. They observed that with increasing the grain size, the band gap shifts to from 3.4 eV to 3.2 eV. Optical properties of $TiO_2$ thin films synthesized by sol–gel process [12], hydrazine processes [13] have been reported by several investigators.

In the present study, we have mainly focused our attention on substrate-type-dependent physical properties of $TiO_2$ films; apart from these investigations, oxide films are synthesized by sol–gel method because of several advantages, such as low processing temperature, homogeneity, possibility of coating on large area substrates, and the most important cost effective. Unlike physical vapor deposition (PVD) or chemical vapor deposition coating technologies, sol–gel technology does not require any high vacuum equipment. Sol–gel oxide films have many applications as func-

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tional materials in optical, microelectronics, and opto-electronics and for the purpose of corrosion, scratch, abrasion resistance [14]. In the present study, $TiO_2$ thin films were prepared by spin coating of untreated sol on to uncoated glass and quartz substrates. In this paper we presented the influence of annealing temperature on the structural, morphological and optical properties of $TiO_2$ thin films.

## 2. Experimental details

The deposition of $TiO_2$ films was accomplished by sol–gel technique at ambient room temperature. These films have been prepared by dissolving the titanium alkoxide precursor, i.e. titanium isopropoxide $[Ti(OC_3H_7)_4]$ in an alcoholic bath. To avoid the early precipitation of the oxides 5 ml of concentrated HCl is used per 100 ml of ethyl alcohol. After addition of the concentrated HCl, solution was stirred vigorously up to 1 h with magnetic stirrer. The obtained clear solution was kept in airtight beaker for 1 h till the gel formation. Then, gel has been spin on coated on various glass and quartz substrates, respectively. The films were preheated in air at 60 °C for 4 h. After preheating, the films were annealed in air at different temperatures like 250 °C, 300 °C and 350 °C for 8 h, respectively.

A Shimatzu SPM-6000 X-ray diffractometer with Cu Kα radiation was employed to study the crystallographic structure of the deposited $TiO_2$ thin films at ambient room temperature. The XRD pattern of the films deposited on transparent substrates has been recorded in scan ranges of $2\theta$ between 10° and 70°. AFM images were recorded using the Nanoscope IIIa scanning probe microscope in a contact mode. The optical transmittance was measured by single beam spectrophotometer (Ocean Optics, USA) after annealing at different temperatures. The optical constants like refractive index and extinction coefficients were estimated by envelope technique [15].

## 3. Results and discussion

The visual observation of as-prepared and annealed films was uniform, compact and pinhole free. The $TiO_2$ films were strongly adherent to the substrate and free from pinholes and visible cracks.

### 3.1. Structural studies

X-ray diffraction (XRD) technique has been employed to identify the structure of the films. The XRD patterns recorded for the $TiO_2$ films deposited on glass substrate as deposited and annealed at 350 °C are shown in Fig. 1. It is clear from Fig. 1 that before annealing, no diffraction peaks of $TiO_2$ have observed indicating that the film is amorphous. Broad hump in the XRD pattern is characteristic of amorphicity and it is seen in all the samples, in the low $2\theta$ region extending from 15° to 40°, irrespective of the annealing temperature/duration. This broad hump defines an amorphous phase in these films and is assigned to the underlying glass substrate. Also big hump recorded from $2\theta = 20°$ to 40° indicates the presence of glass substrate [16]. However annealing at 350 °C, two sharp diffraction peaks at $2\theta = 28.37°$ and 47.35° are observed corresponding to inter-planner spacing of 3.14 Å and 1.89 Å indicates (1 1 1) and (2 2 0) planes. These peaks clearly indicate the presence of anatase (crystalline) phase of $TiO_2$. The threshold for the appearance of crystallinity in the films seems to be in the temperature range of 250–300 °C. The films treated at 350 °C and above are thus characterized by the existence of a crystalline phase [17]. The crystalline phase is identified as the anatase phase ($a = 0.37$ nm, $c = 0.95$ nm) with the single observed diffraction peak oriented along the (1 1 1) crystallographic plane, which corresponds well with the JCPDS data file number 21-272. Annealing $TiO_2$ films in the range from 250 °C to 500 °C, the intensity of the diffraction peaks has been increased, which inferred that $TiO_2$ film becoming more crystalline. The crystallite size is increased as a function of annealing temperature. The

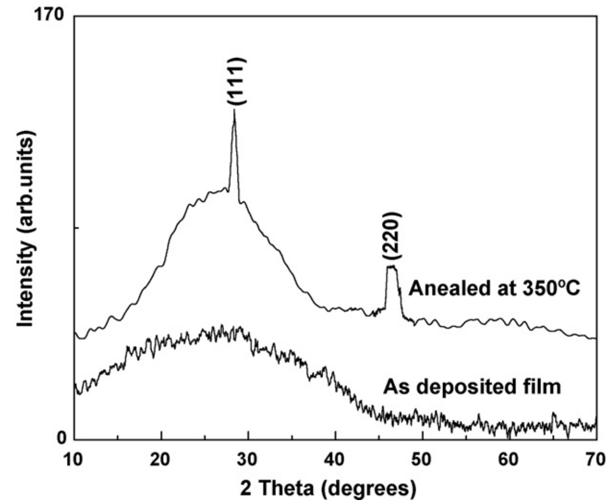


**Fig. 1.** X-ray diffraction patterns for $TiO_2$ films for glass substrate annealed at 350 °C.

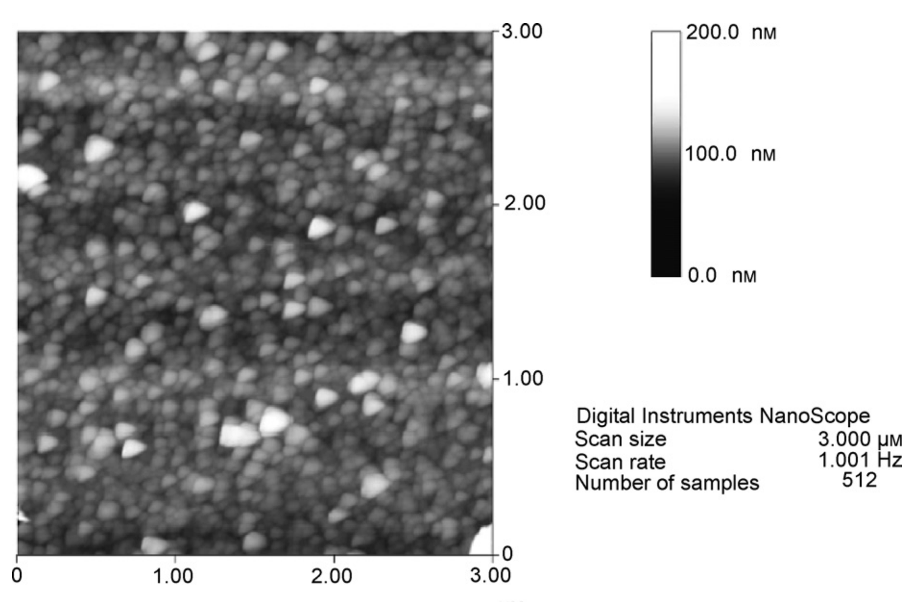


**Fig. 2.** The morphological AFM image recorded of $TiO_2$ film on glass substrates annealed at 350 °C.