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TiO_2 Thin Film's Fabrication and Characterization in Response to Heat Treatment

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ABSTRACT

In this study, substrates of glass were used for the deposition of transparent nanostructured thin layers of Titanium dioxide (TiO_2) using a spin-coating system, and the solution was processed by sol-gel process. TiO_2 sol and films were prepared with TTIP, hydrochloric acid, DI water, and ethanol. Here is the current work, these thin films were analyzed for various annealing treatments at 300°C, 400°C, 500°C. The various attributes of films such as structural are described by X-ray diffraction (XRD) and RAMAN spectroscopy, morphology, and topography are studied by SEM and AFM, and optical properties are examined by UV-Vis spectroscopy. The direct energy bandgap estimated for the TiO_2 films is 3.65ev, 3.71ev, and 3.75ev after heating at 300°C-400°C-500°C. The initial crystalline phase (anatase) of TiO_2 shows up after 400°C for the four layers which are confirmed by XRD and RAMAN studies. At high temperatures, brookite and rutile crystalline phases are also found with the anatase phase. The attained films are translucent in the wavelength range between 380-700nm and blurred in the 100-380nm range.

Keywords: Sol-gel, Spin coating, Raman spectroscopy, SEM, AFM, etc.

INTRODUCTION

Environmental improvement with TiO_2 photocatalyst is receiving huge attention today because of the rise in environmental issues[1]. TiO_2 is a suitable material Because of many prime physical properties that are required for thin film applications. TiO_2 also has prime chemical, optical, and electrical properties, making it useful in a variety of optical applications, including-gas-sensors[2], multiple-layer optical filters[3], photocatalytic water purification[4], planer waveguides[5]. TiO_2-based solar cells (especially-DSSCs) are a popular area of exploration due to their economical, easy manufacturing, environment friendly, and comparatively good energy conversion efficiency[6]. TiO_2 shows good transmittance, high bandgap, high dielectric constant, chemical stability, low cost, non-toxicity, and the capability to be readily doped with ions[7-9].

Because of its importance in applied physics, we can use various techniques in the TiO_2 thin film preparation like chemical vapor deposition

(CVD)[10], sputtering[11], and sol-gel method[12]. The condition of synthesis and chemistry of the surface will affect the TiO_2 thin film stability. Herein, the sol-gel procedure was adopted because it is simple and reproducible[13].

The Sol-gel procedure has several advantages in comparison to other approaches. The Sol-gel procedure shows excellent control of the chemistry, purity, homogeneity, and crystalline phase because of its simple use and economical machinery. The sol-gel method can retrieve new morphology and new physical properties[14].

The properties of TiO_2 thin film can be modified by different heat temperature treatments. When we increase the temperature, the particle size of TiO_2 increases, resulting in precipitate formation[15]. Usually, the initial crystalline phase (anatase) of TiO_2 is secure up to 600°C, it transforms into the rutile phase at a higher temperature, which has less photoactivity for solar cells. This conversion takes place at about 700°C temperature[16]. By doping metallic ions in varying ratios, we can influence the phase conversion from anatase to rutile and the band-gap energy of TiO_2. We can control band-gap energy and the anatase to the rutile phase transition of TiO_2 by doping metallic ions in various ratios. The factors impacting the stability of the doped TiO_2 are oxidation state, bonding of dopant, and ionic radius, it also improves the photocatalytic activity[17].

To enhance the qualities of solar applications, the current study aims to synthesize and characterize multiple TiO_2 thin film properties, such as its makeup, morphology, and optics, at 3 different annealing temperatures: 300, 400, and 500°C. We prepared TiO_2 sol using the sol-gel method, and we applied TiO_2 to plain substrates made of glass using the spin coating technique. The optical, morphological, and structural outcomes have been analyzed for the photovoltaic device's stability, performance, and capacity.

EXPERIMENTAL

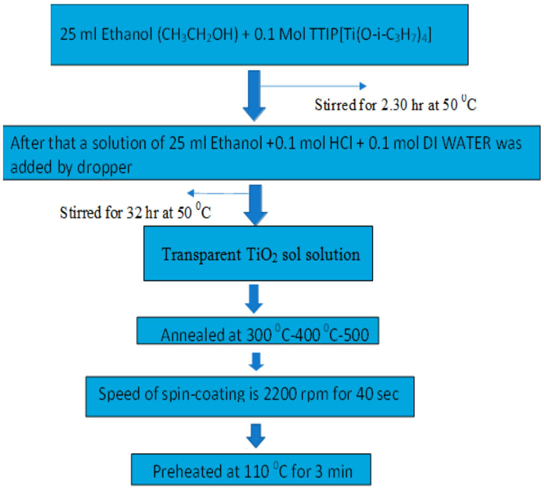
Cleaning process of the glass substrates

We cleaned simple glass substrates sequentially in ethanol, isopropanol, acetone, and then in Deionized water for 10 min each. Substrates were kept under Deionized water before use.

Chemicals

TTIP[$Ti(O\text{-}i\text{-}C_3H_7)_4$], ethanol ($CH_3CH_2OH$), HCl ("Hydrochloric Acid"), and DI water all materials obtained from CDH Pvt. LTD, Daryaganj, Delhi. All the materials are AR grade for the preparation of TiO_2 sol.

Solution Preparation Methodology



Firstly, we take 25 mL Ethanol (CH_3CH_2OH) and 0.1 Mol TTIP [$Ti(O\text{-}i\text{-}C_3H_7)_4$] in a beaker Stirred for 2.30 h at 50°C. A solution of 25 mL Ethanol+0.1mol HCl+0.1 mol DI WATER was added by dropper and Stirred for 2.30 h at 50°C. Then we received a Transparent TiO_2 solution. After that, the prepared solution was spin-coated onto a non-conducting glass substrate at 2200 RPM for 40 second. The deposited TiO_2 thin films have been baked on a hot plate at 110°C for 3 min to remove the solvents and other impurities. After that heat the baked film at 300°C, 400, and 500°C temperature for 30 minute.

Characterization Methods

The X-rd machine (Panalytical X Pert Pro) was employed to the microstructures of the TiO_2 nanocomposites at a temperature of 22°C. The crystal size is evaluated using Scherrer's equation. The FESEM (Nova Nano FE-SEM 450) investigated the surface morphology and chemical configuration. Atomic force microscopy (AFM) having a Multimode Scanning Probe Microscope (Bruker) was employed to investigate the topographical feature.

The absorbance and transmittance measurements of films were analyzed as a sample and non-conducting glass as a standard using UV Spectrophotometer-LAMBDA-750-UV-Vis-NIR. Raman spectroscopy (STR 500 CONFOCAL MICRO) was employed to determine the Raman shift.

Chemical composition

Spin-coated TiO_2 thin films have undergone an energy dispersive spectroscopy (EDS) analysis to ascertain the presence and reveal the chemical makeup of components. The EDS spectrum shows four principal peaks, three for Ti and one for O. The existence of Ti and O materials, as well as their atomic percentages, were verified by EDS analysis. According to EDS analysis, the highlighted atomic concentration in thin films of TiO_2 matches the predicted proportion of atoms at 500°C annealing temperature. The EDS plot is revealed below in Fig. 1. Table 1 comprises TiO_2 thin film EDS data.

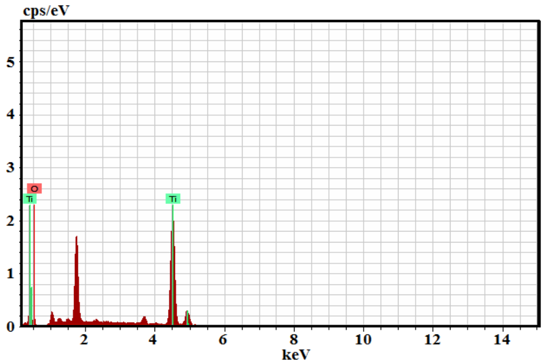


Fig. 1. Chemical composition of TiO_2 thin film annealed at 500°C

Table 1: Composition of TiO_2 in Atomic % of composition

Elements	Atomic %	Weight %
Ti	38.57	64.67
O	62.78	36.06

Structural study

X-Rd patterns have been applied to examine the crystalline phase and size of the crystallite of the deposited nanostructured thin film of TiO_2 at various annealing temperatures of 300°C, 400°C, and 500°C. At the post-annealing temperature of 300°C, we did not get any peak, and it shows an amorphous graph. After that, when the annealing temperature goes to 400°C, the X-rd pattern shows a single peak at 2θ = 250.3635'. It is identified as the anatase phase at the peak (101).

The anatase phase of the peak (101) becomes sharper with the increase in the heat treatment. that shows that crystal size is increasing concerning increasing in annealing temperature. The anatase phase starts to transform into the rutile and brookite phase gradually when we increase the annealing temperature[18].

At 500°C annealing temperature, X-rd spectra show three peaks at 2θ of 25.26920, 37.79280, and 48.00080, which correspond to the lattice planes (101), (004), and (200). The blend of both anatase and rutile phase structure in the final TiO_2 film has been analyzed. In this mixture, the anatase phase has more influence because of the high activity of photocatalysis[19].

Table 2: The crystalline size has been increased with the increase in heat treatment as can be seen in Table (2)

Annealing temperature	Crystallite Size(nm)
400°C	2.10
500°C	3.16

Here we evaluate crystal size(D) by Scherrer's equation:

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

D indicates the average of the crystalline, k represents the shape factor, λ signifies the Cu-Kα x denotes ray wavelength, β indicates the FWHM ("Full Width Half Maxima"), θ presents the Bragg-angle.

The average crystallite size of TiO_2 thin film made using the sol-gel methodology and accumulated by spin coating process at 2000 rpm for 30 sec. came out to be 2.10nm at 400°C and 3.1601nm at 500°C.

Dislocation density (ρ)-Williamson and Smallman's formula (e) was utilized to determine the θ present in the TiO_2 thin film.

$$\theta = \frac{1}{L^2}$$

The determined θ value for TiO_2 thin film is 0.2267nm^{-2} and 0.07672nm^{-2}.

The Raman spectra display distinct peaks linked to the attendance of TiO_2 in anatase and brookite phases at annealing temperatures of 400°C and 500°C. Bands about 153 and 193 cm^{-1} are ascribed to the TiO_2 anatase phase in these spectra[20].

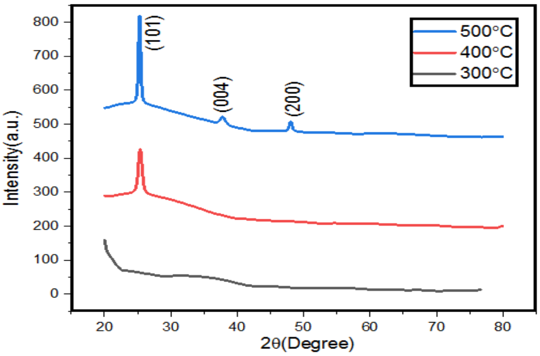


Fig. 2. XRD pattern of TiO_2 films annealed at various temperatures

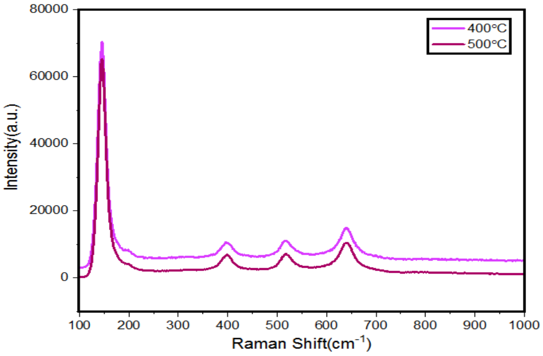


Fig. 3. Raman spectra of TiO_2 thin film at different temperature

Investigation of optical characteristics

The optical features of thin films of TiO_2 can be analyzed with Transmittance spectra (Fig), absorbance spectra Fig. 4, and reflectance spectra Fig.5(a) from 200 to 800nm which are displayed. The transparency on average is 80% in the visible range. The film transmission aggrandized moderately in the influence of annealing temperature in the near-infrared region. An incisive decrease is observed in each absorbance spectra at 300–345nm probably because of imperfection in the crystallinity of the material. The Tauc expression is applied to compute the energy band gap (Eg)[21].

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where α, h, E_g, A, and n have their usual meaning.

A straight line with an intercept to the X-axis is expected to offer the optical band gap in its direct form on a graph between $(\alpha h\nu)^2$ and h . The curve between $(\alpha h\nu)^2$ and $h\nu$ is displayed in Fig. 5(b). The essence of acquired data shows that TiO_2 thin films have a direct band-gap-gap and when the annealing temperature was increased the direct band-gap was decreased. This acquired band gap was higher than the proclaimed optical band gap for single-crystal 3.2ev. The large optical band gap value obtained for spin-coated TiO_2 thin film might be because of the quantum size impact and size of finite crystallite[22].

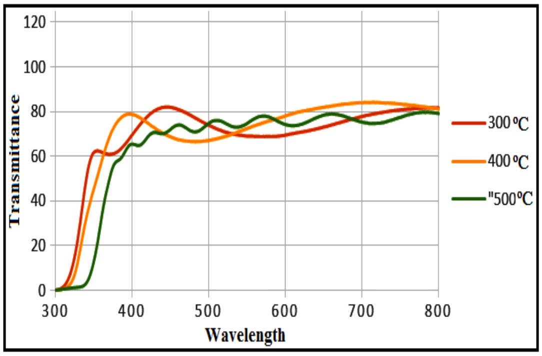


Fig. 4. UV transmittance spectrum of the TiO_2

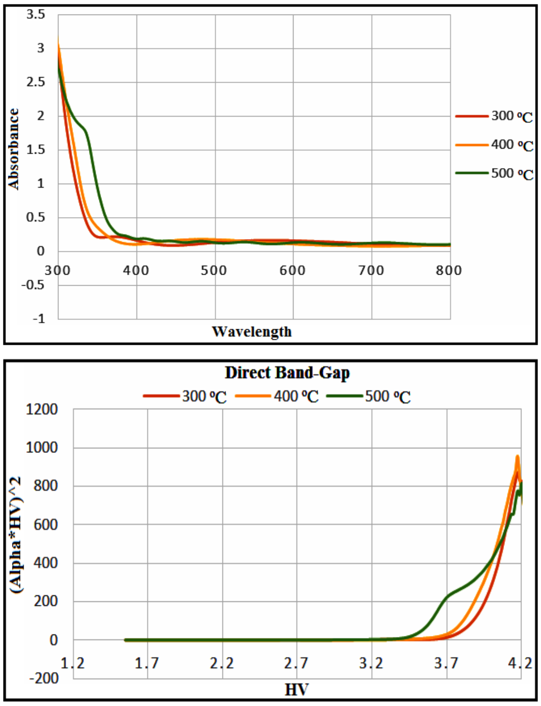


Fig. 5. UV absorption spectrum of the TiO_2

Surface morphology study

SEM was employed to investigate the shape of the surface (surface morphology) and the dispersion of pores of the developed films. Its images show particles are divergent, spherical, and extended, with large particle size distribution. SEM investigates morphological changes of annealed TiO_2 thin films from 300°C, 400°C, and 500°C confirming that the surface morphology of the film has been modified with the annealing temperature. Fig. 6 displays the SEM images in the top view, and it is examined that the larger particles are made of smaller fragments, the distance between nanoparticles reduces with the rising temperature, and thin films will be more closely packed. The SEM analysis verifies that annealing temperature treatment plays a vital role in the morphology of TiO_2 thin film, thus the crystallization of layers. Above, X-rd data and AFM also support the SEM observations that the size of crystallite increases from 300°C to 500°C as a result of densification.[23]

AFM is utilized to check the surface morphology mitigation and evaluation of TiO_2 thin films at 500°C annealing temperature. AFM images at 500°C Fig. 7 show that the grain agglomeration is in a satisfactory state.

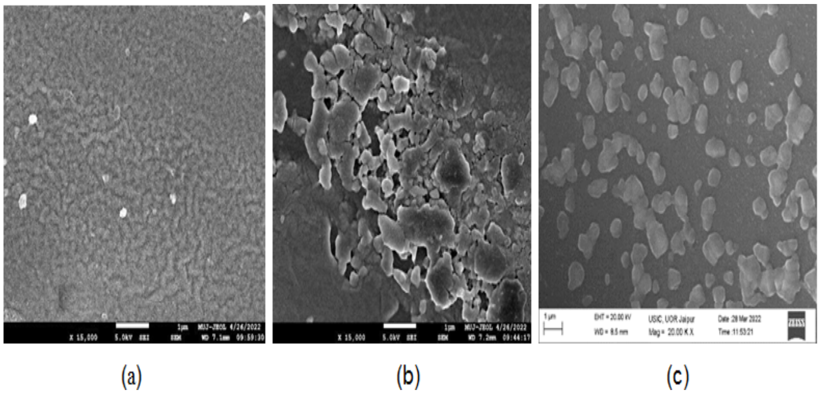


Fig. 6. SEM micrographs of the TiO_2 at post-heat treatment (a) 300°C (b) 400°C & (c) 500°C

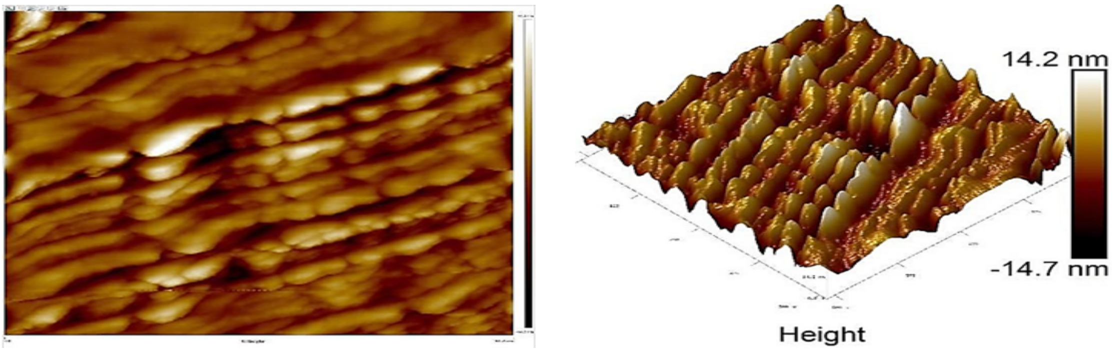


Fig. 7. AFM images of the TiO_2 thin film annealed at 500°C

CONCLUSION

This study describes the formation and characteristics of the TiO_2 thin films employing a simple and economical method: sol-gel spin coating methodology. As it generates samples with high homogeneity and repeatability, the sol-gel method is acknowledged as one of the most straightforward procedures for preparing TiO_2 thin films and the most effective in terms of layer quality. The deposition was carried out at a temperature of 22°C and post-annealed at distinct temperatures of 300°C-400°C-500°C. The influence of temperature on the features of TiO_2 is discussed in this study.

The X-rd pattern reveals an amorphous graph at an annealing temperature of 300°C, it shows an anatase phase around 400°C. Furthermore, at a higher annealing temperature (500°C), it shows the presence of both initial phases (rutile-anatase) of TiO_2. The Raman spectra also help this fact.

The SEM microscopy shows no breaks in the film, which is made up of microscopic flaky clusters at 300°C heat treatment. Further, grain size increases with an increase in heat treatment. The study of UV-Vis spectra reveals that absorbance decreases abruptly around wavelength 340-345nm and the band gap increases gradually with increasing temperature.

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Conflict of interest

The author declare that we have no conflict of interest.

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