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Review of morphological, optical and structural characteristics of TiO_2 thin film prepared by sol gel spin-coating technique

Muhammad Bilal Tahir*, Khalid Nadeem, M Hafeez & Shamsa Firdous

Department of Physics, University of Gujrat, Gujrat 50700, Punjab, Pakistan

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Optical, structural and morphological properties of titanium dioxide (TiO_2) deposited by spin coating method have been reviewed in the current work. Sol–gel spin coating is a cost effective and versatile technique due to intellectual properties like simple instruments, easy preparation technique, and less time consuming. In this method, compound in the form of metal oxides is liquefied in a specific liquid in order to bring it back as a solid in a skillful manner. Study of metal oxide thin films have valuable applications in numerous semiconductor devices such as optoelectronics devices and solar energy converters etc. X-ray diffraction (XRD) analysis has been used for studying TiO_2 thin films and scanning electron microscopy (SEM) analysis has been applied for morphological investigation and to prove the nanosized structure. Optical and structural properties have been studied as a function of the annealing temperatures. XRD analysis reveals that the films crystallize in orthorhombic brookite phase. Moreover, UV-visible has been used to investigate the optical properties of material. XRD characterization indicates that crystalline structure of TiO_2 thin films improves with increasing annealing temperatures which confirms the anatase form of TiO_2 thin film. Optical band gap is significantly dependent on the annealing temperatures. The refractive index may increases with increase of crystallite size. The TiO_2 film annealed at 400 °C shows high refractive index 2.52 at a wavelength of 335 nm. Moreover, optical band gapes of thin film vary approximately from 3.3 to 3.46 eV which show strong relation with annealing temperature.

Keywords: Spin coating method, XRD analysis, Annealing temperature, Refractive index

1 Introduction

Semiconductor metal oxide-TiO_2 thin films have become very attractive candidates for numerous fields of industrial, and technological applications including varistors, thin-film solar cells, gas sensors, ultraviolet (UV) detectors, and thin film transistors particularly due to wide band-gap energy at room temperature and high mechanical properties and thermal stability. In modern era of technology, vast deal of consideration being conferred upon the making of low-priced thin films, due to their high varying characteristics like characteristics consist of heat reflective windows, resistivity, and photovoltaic, photo thermal and catalytic properties[1-5]. It has been reviewed that nano-structured based TiO_2 thin films deposited on glass substrate are very effective in optical coatings, electronic devices, catalysis, gas sensors, and DSSC[6,7]. TiO_2 is broadly used substrate for protective and optical applications as well due to high transparency in the visible-region, chemical stability in aqueous solution and excellent mechanical durability[8]. TiO_2 has very unique properties such as it is nontoxic, inexpensive, highly photoactive and easily synthesized material. TiO_2 is found in three phases, i.e., rutile, anatase, brookite but out of these phases rutile has stable form. It has also high refractive index up to 2.7, high dielectric constant, wide band gap (E_g> 3 eV) and high chemical and photo stability. Due to high refractive index and excellent insulating properties it is mostly used in electronic device applications and protective layer for integrated circuits[9,10].

TiO_2 thin films may be synthesized by numerous sophisticated techniques such as chemical vapor deposition (CVD), sputtering, electro spray deposition, spin coating, atomic layer deposition (ALD), cathode arc deposition, dip coater and molecular beam epitaxy[11-13] (MBE). It has been established by research that the preparation technique and processing conditions strongly impact the microstructure and physical properties of the material. Most processes required high energy, involve high temperature, pressure and vacuum for working. On the other hand spin coating method is one of the most simple, cost effective, fast and suitable method for the deposition of thin film on different types of substrates. Spin coating has many advantages over other thin film coating

*Corresponding author (E-mail: m.bilaltahir@uog.edu.pk)

methods; its biggest advantage is that the film thickness is easily changed by switching to various viscosity photo resist or by changing spin speed[14-16]. The spin coating method is one of the most efficient methods to produces samples with good homogeneity.

In this paper, it has been reviewed that sol-gel coating has become beneficially for preparing different variety of both organic and inorganic materials. By sol-gel spin coating, researchers can easily prepare transparent, multi-component oxide layers of different composition on many types of substrate due to its low processing temperature, capability of large coating area, good homogeneity, potential for cost-effective mass production, composition control and easy to display on substrate. Moreover, different properties including morphology, optical and structural have been investigated by SEM, UV-vis, and XRD, respectively, with reference to various parameters like rpm speed, time, solution preparation method, temperature and environment etc.

2 Methodology

Spin coating technique has been studied for the preparation of smooth and homogenous thin films on glass substrates. In this process, drop/s of synthesized solution was pour down on the surface of glass material via syringe. The glass substrate was fixed on a target holder which is then rotated at specific rpm speed (spin coater apparatus) in order to spread the solution uniformly by centrifugal force. Centripetal acceleration will cause most of the resin to spread to, and eventually off, the edge of the substrate, leaving a thin film resin on the surface. The thickness of thin film significantly depends on different parameter including rpm speed, time, solution quantity, and ambient environment. Therefore rotation of the substrate holder is continued until desired film thickness is achieved for a particular application. The deposited solution is usually volatile, and instantaneously evaporates. So, the higher the spinning rpm, thinner will be film[17]. This method is extensively used in micro-fabrication to createthin films with thicknesses below 10 nm. More precisely one can easily understand the spin-coating process in a following four different stages of the process:

(i) Deposition of coating solution onto the substrate/ target/wafer
(ii) Target holder is accelerated up to its final and desired rotation speed
(iii) The target is spinning at a constant rate and fluid viscous forces dominate the fluid thinning behavior
(iv) Target is spinning at a constant rate and solvent evaporation governs the coating thinning behavior.

After evaporation of the whole solvent, a solid film is generated. It is worth mention that to get homogeneous films, several factors are needed to be taking into consideration. These factors include evaporation rate, viscosity, concentration, rpm speed, time and acceleration[18,19]. TiO_2 thin film deposited on to typical ultrasonic glass substrate of 2.5 cm×2.5 cm, 1.35 mm thickness by using solution of sol-gel, i.e., mixture of titanium tetra isopropoxide $\{Ti(OC_3H_7)_4\}$, ethanol and acetic acid using spin coating machine. Ultrasonic cleaned glass may take with the help of pure water for 30 min and then cleaned with acetone. The basic process of preparation of TiO_2 thin film is shown[20] in Fig. 1. P. Malliga *et al.*[20] tells that TiO_2 prepared thin film is then subjected to XRD, UV-visible, photoluminescence and SEM-EDAX analyses. Thin film through coating cycle treated by X-ray diffraction using X'PERT PRO X–ray diffractrometer which was operated at 40 kV and 30 mA with $CuK_{\alpha 1}$ radiation of wavelength 1.5407 Å. Surfest SJ–301 (Stylus profilometer) is used for measuring thin film thickness. Optical properties are studied by UV-visible range spectrophotometer with xenon lamp as the light source at room temperature at an excitation wavelength of 410 nm. Quanta SEG- 200 FESEM and Bruker EDX have been reviewed to study surface morphology and elemental analysis, respectively[11]. AFM was used to investigate the surface topography of samples using

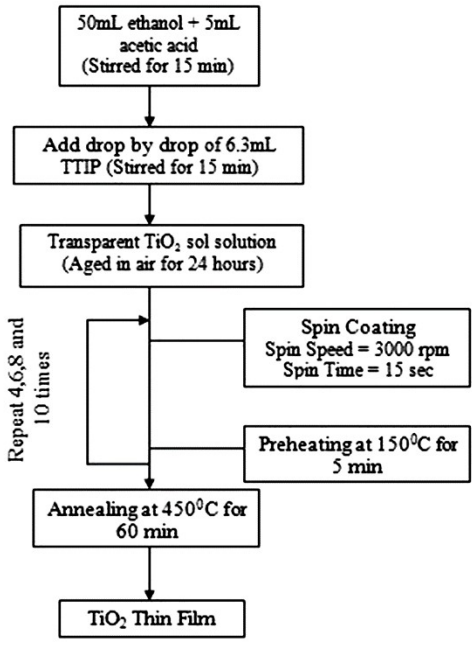

Fig. 1 — Flow chart for preparation of TiO_2 thin films[20].

a Veeco Multi Mode V AFM system at room temperature[21]. Isrihetty Senain *et al.*[22] suggested that the TiO_2 solution can be prepared by adding titanium butoxide along with glacial acetic acid, ethanol, deionized water and triton.

3 Results and Discussion

3.1 X-ray diffractometer analysis

Figure 2 shows the XRD pattern of TiO_2 thin film annealed at 300 °C and 400 °C for 2 h. The observed XRD patterns are compared with standard JCPDS data file (File Nos. 84-1750), matching the observed 2θ values with that of standard ones. The film annealed at 400 °C showed diffraction peaks at 2θ=25.45°, 31.39° and 66.45° which were indexed as (110), (111) and (023), respectively[12]. The XRD pattern of TiO_2 film annealed at 300 °C does not exhibit clear peaks indicating that the film is amorphous in nature. The presence of peaks in the X-ray diffraction pattern of film annealed at 400 °C revealed the formation of single phase orthorhombic brookite TiO_2 film. Crystallite size was calculated by using Scherrer's formula[12]:

$$D = 0.9\lambda/\beta\cos\theta \quad \ldots (1)$$

where θ is the Bragg angle, β is the full width and λ is the wavelength of the incident X-ray. The crystallite size calculated from the XRD peak (111) with 2θ=31.39° at an annealing temperatures of 400 °C was found to be 67 nm. The dislocation density of the crystal gives information about the crystal structure[22]. The smaller the dislocation density better is the crystallization of the film. Dislocation is an imperfection in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. The dislocation density (δ) is estimated by the Williamson and Smallman's relation, respectively, dislocation density is a measure of lattice imperfections and defects. The peak at 2θ= 25.071°, 25.504°, 25.44° and 31.72° confirms the anatase phase of TiO_2 thin film.

3.2 SEM analysis

Figure 3(a) gives the surface morphology of the SEM pattern recorded for TiO_2 thin film annealed at 300 °C and 400 °C. SEM photographs reveal that the thin films are uniform, crack free and good coverage of

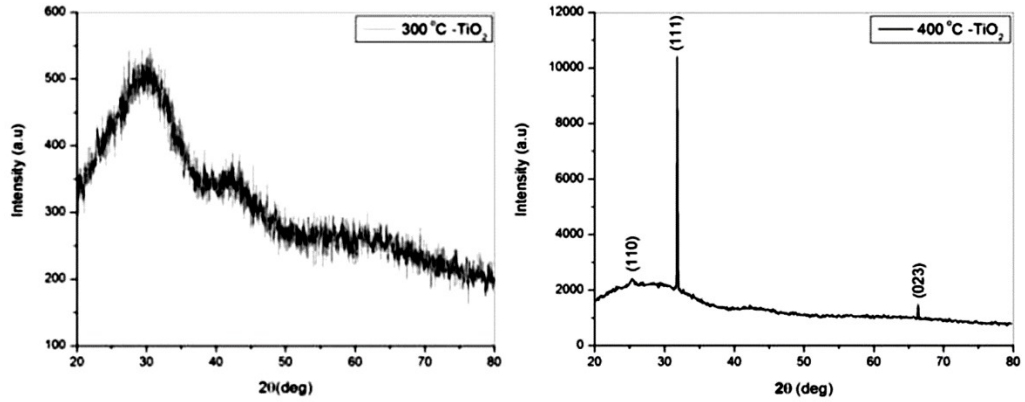

Fig. 2 — XRD patterns[21] of the TiO_2 film at 300 °C and 400 °C.

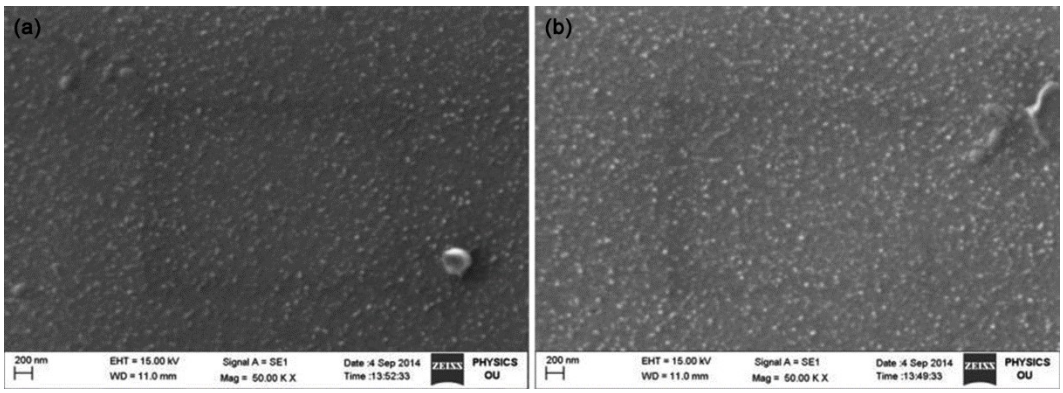

Fig. 3 — SEM micrographs[22] of TiO_2 films at (a) 300 °C and (b) 400 °C.

the glass substrate surface. The particles are seemed to have a spherical shape. The average diameter of the particles was found to be from 10-70 nm. From Fig. 3(b) it is clear that the morphology of TiO_2 film before and after the annealing processes was changed. The surface roughness increases from 0.341 nm to 1.690 nm after the annealing process at the described conditions. Larger surface can be due to the larger grain sizes of nanostructured TiO_2 film, as shown in figure. The rough surface of film increases from 0.341 to 1.690 nm after the annealing process at applied conditions. Large rough surface is due to larger grain size of nanostructured of TiO_2 film, as shown in Fig. 3 (b). Moreover, these experimental results are confirmed by EDX and AFM as well. Energy dispersive X-ray spectrum of TiO_2 thin film is shown[23,24] in Fig. 4. The EDX analysis confirmed the presence of Ti and O elements in the deposited films[14]. It is noted that the roughness for TiO_2 was 0.625 at 70% quantity of ethanolusing AFM images of thin film given in Fig. 5. It is also observed that roughness could be increased to 1.690 at 20% amount of ethanol approximately.

3.3 Optical properties

Figure 6(a) shows the optical spectra of spin coated TiO_2 thin films annealed at different temperatures[19].

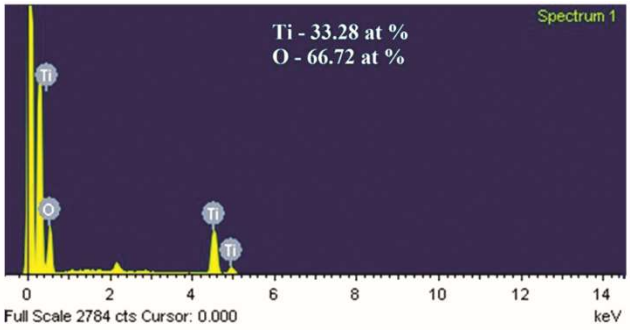

Fig. 4 — EDX analysis[19] of TiO_2 thin film at 400 °C.

It has been observed that transmittance decreases with an increase in annealing temperature due to the rougher surface, the light scattering is greater and, respectively, the transmittance is lower after 400 °C annealing. TiO_2 films exhibit high transparency ~97% at a wavelength of 405 nm. The transmittance maxima decreased with the annealing temperature. The transmittance maxima shifted to longer wavelength side at 400 °C. This is an indication that the size of crystal was increased with the increase of annealing temperature especially at 400 °C. The data shows that as annealing temperature increases, the refractive index must be changes. It increases with increase in annealing temperature, from 2.42 to 2.52 at a wavelength of 335 nm. The highest refractive index of TiO_2 film reaches to 2.52, which was close to the bulk TiO_2. When thin film annealed at 400 °C the rapid increase of refractive index might be due to the thermal induced growth of the crystallite size[25,26]. The refractive indices were found to increase with an increase in the crystallite size, whereas the band gap energies were decreased due to increase of annealing temperature[17]. The transmission and reflectance spectra are shown in Fig. 6. It has been considered that film is highly transparent which is from in the visible range with an average transmittance, i.e., about 85% but it decreases when the number of coatings increases and it is due to increase in film thickness. It is observed from optical absorbance spectra that with increasing annealing temperature absorbance of TiO_2 thin films increase. This is due to increasing of crystalline size which increases the surface roughness. These optical spectra revealed that transmittance decreases with increasing annealing temperature due to increasing surface roughness and crystalline size. The film which is annealed at 300 °C and 400 °C shows a significant decrease in visible light transmittance due to increasing surface roughness which scattered more light.

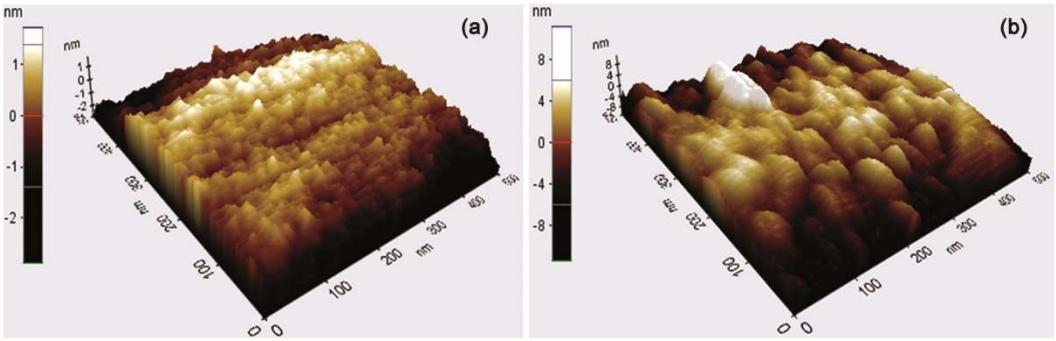

Fig. 5 — AFM image of TiO_2 thin film (a) before and (b) after annealing[21].

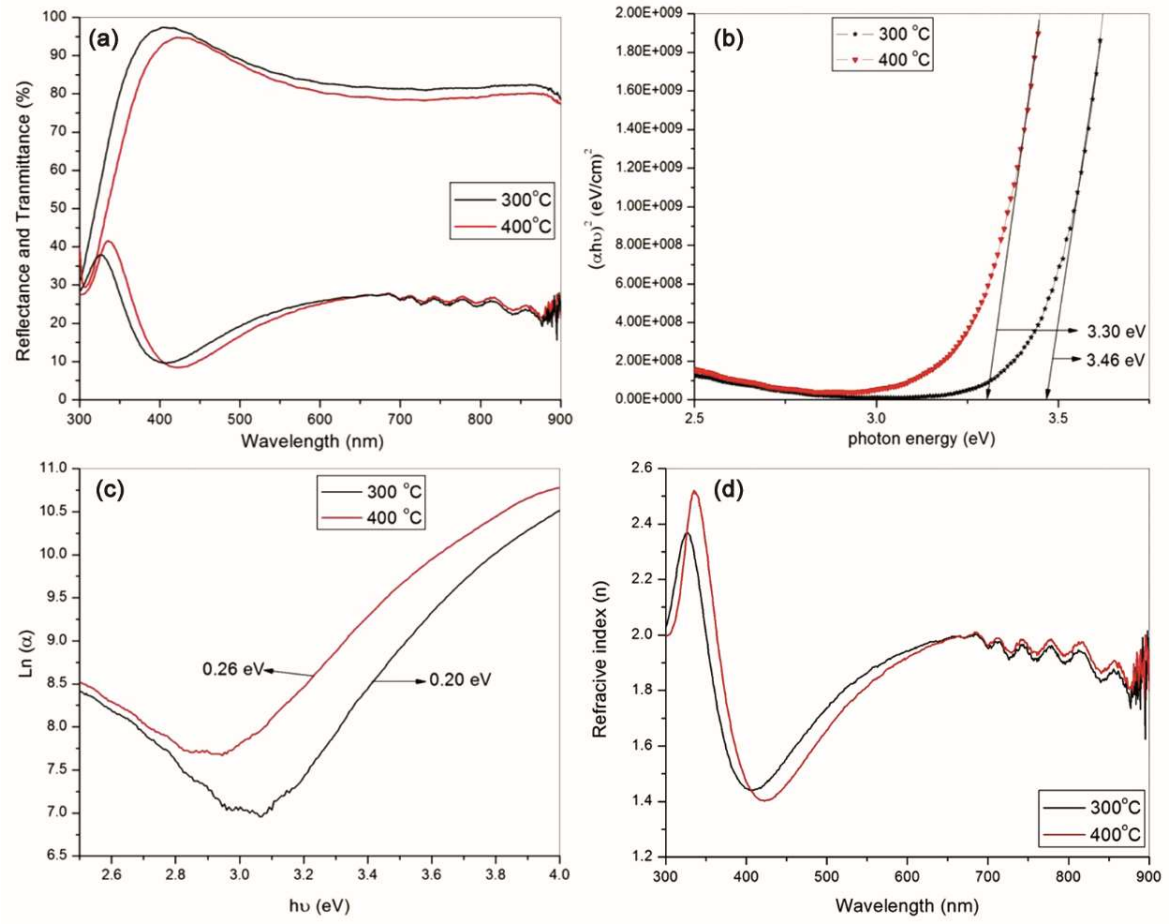

Fig. 6 — (a) Transmittance and reflectance spectra, (b) $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$), (c) plots of lnα versus photon energy ($h\upsilon$) and (d) plots of refractive index versus wavelength, of TiO_2 thin film annealed at different temperatures.

4 Conclusions

It has been concluded that sol-gel coating technique employed excellent end resulted better than any other techniques used for deposition of thin films. It is observed that XRD analysis provides the size of prepared crystal which increases, at same time micro grain and dislocation density decreases. The diffraction pattern of TiO_2 thin film exhibits the diffraction peaks characteristics anatase phase of TiO_2 with increasing annealing temperature. XRD characterization indicates crystalline structure of TiO_2 thin films improved as annealed at higher temperatures which confirm the anatase form of TiO_2 thin film. Optical analysis revealed that band gap transmittance decreases with reference to annealing temperature. FESEM show morphology and the typical stoichiometric ratio investigated through EDX spectra. Moreover, the end results revealed that thickness of film has high effect on the properties of TiO_2.

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