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Titanium Dioxide Versatile Solid Crystalline: An Overview

Lourduraj Stephen

Abstract

Among the several choices, titanium dioxide (TiO_2) is the most efficient material and has attracted great attention because of its certain specific properties like high permittivity, refractive index, efficiency, low cost, chemical inertness, non-toxicity, photocatalytic activity, photostability and capability of decomposing a wide variety of organic compounds. In the field of dental, orthopedic and osteosynthesis applications, the titanium and its native oxide (titanium dioxide) are used as an implant material. TiO_2 is used in an extremely wide range of commercial applications and research areas including: (i) TiO_2 powder: as a white pigment in paint, plastic, inks, paper and cosmetics; in washing powder, toothpaste, sunscreen, foodstuffs, pharmaceuticals, photographic plates, for creating synthetic gemstones; and as a catalyst. (ii) TiO_2 thin films: for ultra-thin capacitors and MOSFETs due to its extremely high dielectric constant; as humidity and oxygen sensor due to the dependence of its electrical conductance on the gases present; as an optical coating and a material for waveguides due to its high refractive index; as a protective coating and corrosion-resistant barrier; and as a photoanode in solar cells due its photoelectric activity.

Keywords: nanoparticles, titania, sol-gel, spin coating, thin films, electronic, optical, solar cells

1. Introduction

Research in the development of efficient materials has seen significant progress in the last two decades with a large number of research works carried out every year. Improvements in the performance of materials have been largely correlated with advances in nanotechnology. In recent years, the metal oxide nanoparticles are increasingly receiving attention for their wide range of applications in almost each and every field. Concerns regarding metal oxide nanoparticles exist in their chemistry and size and for being non-biodegradable. This poses the rapid distribution of nanoparticles in the environment with potentially harmful consequences.

2. Titanium dioxide semiconducting material

Titanium dioxide (TiO_2) is an n-type metal oxide semiconducting material used in a wide range of common and high-tech applications. It is cheap, chemically stable, non-toxic and bio-compatible. Titania is successfully used as implant material in dental, orthopedic and osteosynthesis applications and its native oxide mostly constitutes titanium dioxide [1]. TiO_2 in the form of nanopowder is used as

a white pigment in paint [2], replacing lead oxide that is toxic, and in toothpaste. In the form of solid thin films, transparent single crystals or its thin films have a high refractive index that makes TiO_2 suitable for optical applications [3, 4]. Multi-layers composed of TiO_2 and SiO_2 are designed to make antireflection coatings in the whole visible range [5, 6]. TiO_2 is widely used for photocatalysis [6]; for example, electrodes made of TiO_2 are used in electrochromic devices [7] and dye-sensitized solar cells [8] etc., and solid-state photovoltaic solar cells with porous TiO_2 layer show promising results [2, 3]. Pd-TiO_2 diodes are used as hydrogen gas sensors [9, 10], and nowadays, TiO_2 can replace ZrO_2 in lambda probes used in the car industry [11]. Most of these applications are due to its n-type semiconducting property and realized with micro- or nano-structured TiO_2 nanopowders or nano thin films.

3. TiO_2 crystal structure

Titanium oxide exists in nature as minerals and it has various structures under ambient conditions: rutile, anatase, brookite and srilankite (this last structure is also called PbO_2 -type TiO_2 or TiO_2 -II) [12–14]. Rutile is a relatively abundant material and its structure is the most stable [13] and also the most studied. Anatase and brookite are extremely rare in nature [10]. TiO_2 thin films are generally amorphous for deposition temperatures $\leq 350^\circ\text{C}$, above which anatase is formed. The most stable crystalline phase, rutile, is formed at temperatures greater than about 800°C . The brookite phase is rarely observed in deposited thin films. The functional properties of TiO_2 films, powders and ceramics are strongly dependent on the phase of the material. Thus, TiO_{2-x} is an n-type semiconductor, in contrast with p-type semiconductors, which contain electron acceptors and where the charge carriers are holes rather than electrons [15]. Substoichiometric TiO_{2-x} is both a poor insulator and a modest semiconductor. Therefore, several attempts have been made either to control the oxygen vacancy concentration or to introduce charge carriers (doping) inside TiO_2 in order to enhance the properties, depending on the needed application. After 50 years, the periodic table was updated by incorporation of new atoms such as Ti and so on [16]. The structural, optical and electrical properties of TiO_2 are reported in **Table 1**.

Polymorph	Anatase	Rutile	Brookite
Structure and space group [1]	Tetragonal I 4 ₁ /amd	Tetragonal P 4 ₂ /mmn	Orthorhombic Pbca
Lattice parameter	a = 3.7923 c = 9.5548 (T = 350°C)	a = 4.5930 c = 2.9590	a = 5.4558 b = 9.1819 c = 5.142
Density (g cm ⁻³) [1]	3.84	4.26	4.12
Refractive index λ = 600 nm [7]	⊥ to c axis 2.55 // to c axis 2.48	⊥ to c axis 2.60 // to c axis 2.89	⊥ to a or b axis 2.57 // to c axis 2.69
Dielectric constant [8–10]	⊥ to c axis 31 // to c axis 48	⊥ to c axis 89 // to c axis 173	78
Band gap (eV) [12, 13]	⊥ to c axis Direct 3.42 // to c axis indirect 3.46	⊥ to c axis Direct 3.04 // to c axis indirect 3.05	3.14
Electron mobility (10 ⁻⁴ m ² /Vs) [14, 15]	crystal: 15–550 thin film: 0.1–4	crystal: 0.1–10 thin film: 0.1	—

Table 1.
TiO₂ properties.

The elementary cells of the TiO_2 crystal structures, phase transition and crystallographic structures of TiO_2 are presented in **Figures 1–3**, respectively. Rutile and anatase, which are tetragonal, are more ordered than the orthorhombic structure. Anatase, which is the least dense structure, has empty channels along the a and b axes.

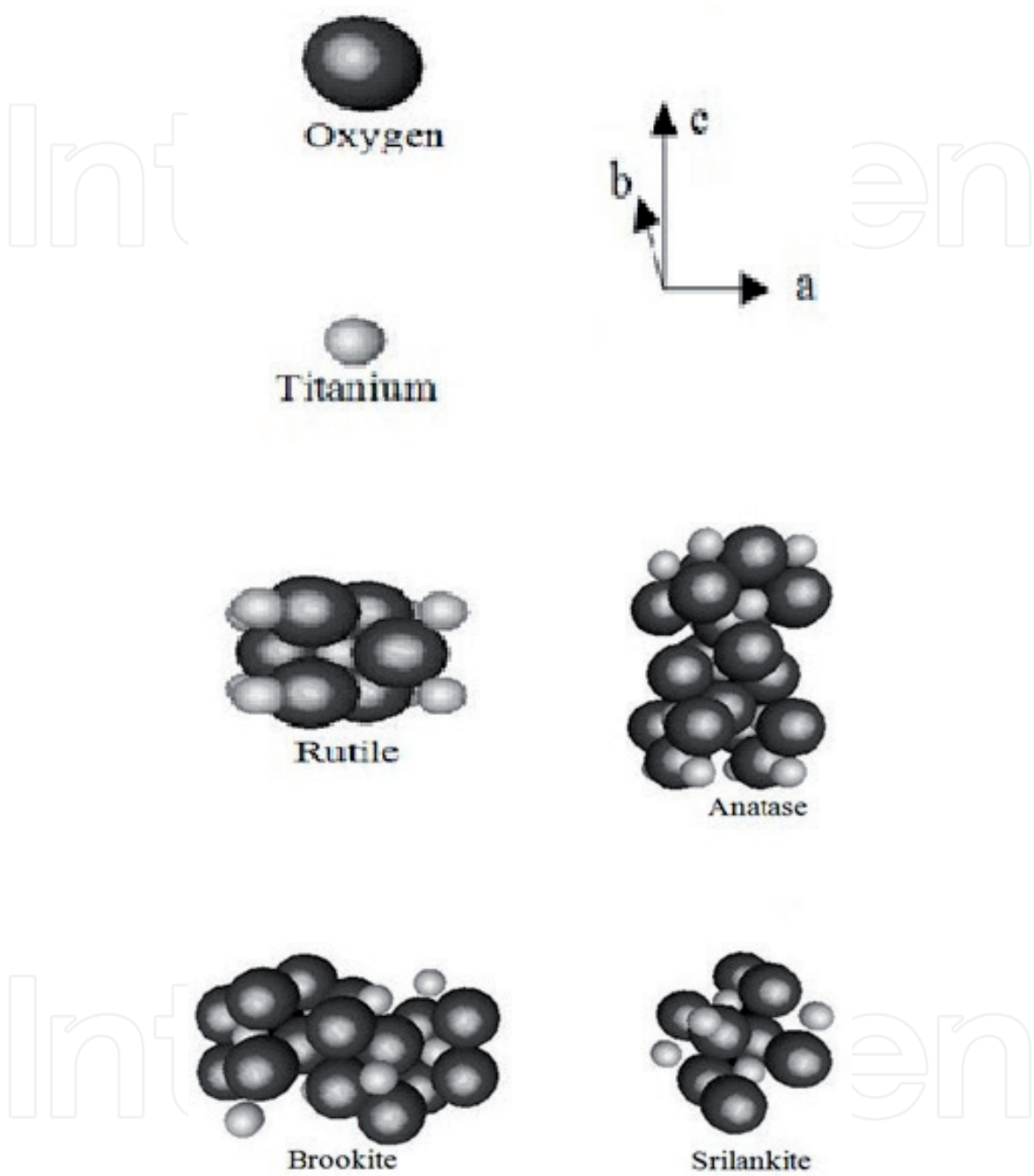


Figure 1.
Elementary cell of TiO_2 polymorphs.

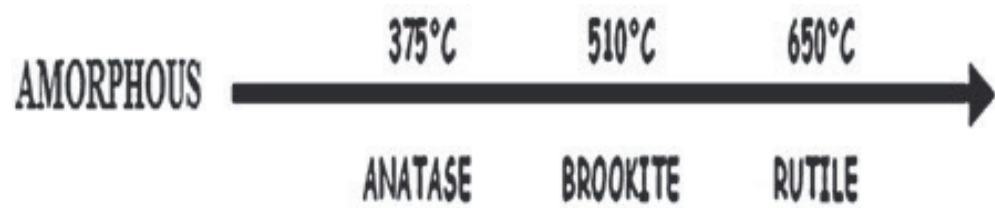


Figure 2.
Phase transition of titanium dioxide.

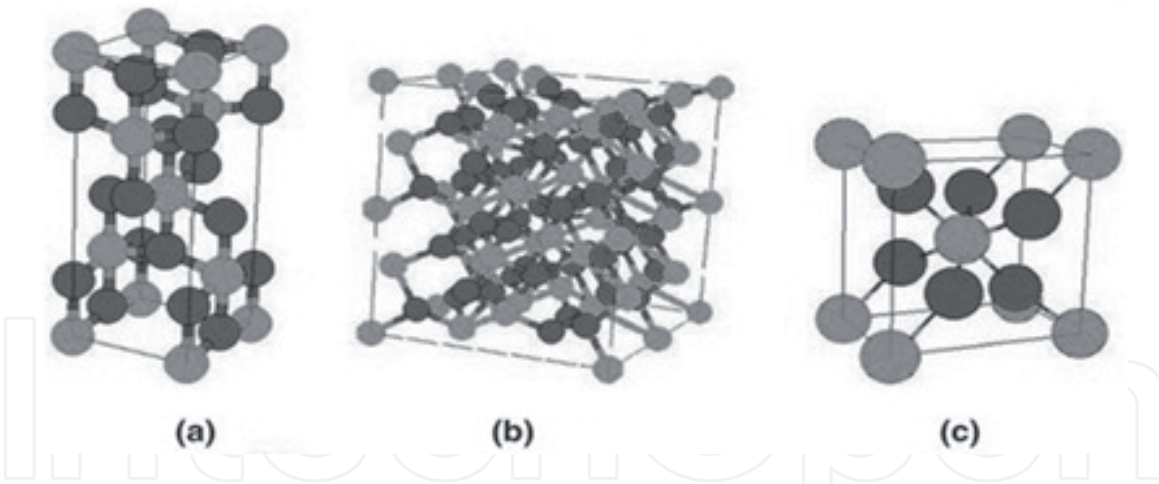


Figure 3.
Crystallographic structures of TiO_2 (a) anatase, (b) brookite, and (c) rutile.

4. Properties of TiO_2 thin films

The performance of TiO_2 thin-film based devices depends on its structural, surface morphological, compositional, optical and electrical properties. It is evident that the improvement of materials properties requires a closer inspection of preparative conditions and also the above said properties of the films.

The physical, optical, electrical and chemical properties of titanium dioxide (TiO_2) depend greatly on the amorphous or crystalline phase of the material. TiO_2 is a complex material with three crystalline phases, two of which are commonly observed in thin films—anatase and rutile. Anatase is commonly observed at film deposition temperatures of 350–700°C, while higher temperatures promote the growth of rutile. Deposition temperature lower than 300°C generally result in the formation of amorphous TiO_2 and it has highest band gap (3.5 eV), low refractive index (1.9–2 at 600 nm) and extinction coefficient. Polycrystalline anatase thin films with an optical band gap (3.2 eV) exhibit a much higher refractive index and slightly increased absorption coefficient. The chemical resistance of amorphous TiO_2 films is poor in many acidic and basic solutions as compared with crystalline structure because of anatase, which is insoluble in many acids and base. The TiO_2 thin films with rutile phase are having extremely higher refractive indices (up to 2.7 at 600 nm) and lower the band gap absorption is still low. The chemical resistance of rutile is excellent, and after annealing at temperatures above 1000°C, it is insoluble in nearly all acids and bases.

Thin films of TiO_2 are used in an extremely wide range of commercial applications and research areas, including the following:

TiO_2 powders and nanopowders: as a white pigment in paint, plastic, inks, paper and cosmetics; in washing powder, toothpaste, sunscreen, foodstuffs, pharmaceuticals, photographic plates, for creating synthetic gemstones; and as a catalyst.

TiO_2 thin films and their derivatives: for ultra-thin capacitors and MOSFETs due to their extremely high dielectric constant; as humidity and oxygen sensor due to the dependence of their electrical conductance on the gases present; as an optical coating and a material for waveguides due to their high refractive index; as a protective coating and corrosion resistant barrier; and as a photoanode in solar cells due their photoelectric activity.

4.1 Semiconductor properties

Solid materials are classified in three groups depending on their electrical conductivity σ . Highly conducting materials are metals ($\sigma > 10^4 \text{ S m}^{-1}$), material

with very low electrical conductivity are insulators ($\sigma < 10^{-8} \text{ S m}^{-1}$), and in-between stand the semiconductors. The main difference between metal and semiconductor is the fact that for metals, the electrical conductivity decreases when temperature increases, while the reverse phenomenon usually occurs in the case of semiconductors. The energy band diagram of a pure semiconductor containing a negligible amount of impurities (intrinsic semiconductor) is characterized by an energy gap (E_G) inside which no electronic states are encountered.

When a semiconductor is doped with donor and/or acceptor impurities, impurity energy levels are introduced. A donor level is defined as being neutral if filled with an electron and positive if empty. An acceptor level is neutral if empty and negative if filled by an electron. The Fermi level for the intrinsic semiconductor lies close to the middle of the band gap (**Figure 4**). When impurity atoms are introduced, the Fermi level must adjust itself to preserve charge neutrality, and the total negative charge (electrons and ionized acceptors) must equal the total positive charge (holes and ionized donors). N-type and p-type semiconductor band diagram is shown in **Figure 4** [17, 18].

4.2 Physical properties

4.2.1 The amorphous-anatase-rutile phase transformations

Amorphous TiO_2 thin films can be deposited at temperatures as low as $100\text{--}150^\circ\text{C}$ [19, 20]. Amorphous TiO_2 does not have a strict crystallographic structure, often incorporates voids within the material, and has a relatively low density. For TiO_2 thin films formed by chemical reaction, the lowest temperature crystalline phase of TiO_2 that can be obtained is anatase. To obtain polycrystalline anatase, the film can be either deposited as amorphous TiO_2 and then crystallized by annealing at a higher temperature or deposited as polycrystalline material directly. The results indicate that the transition from an amorphous to anatase film occurs at about $300\text{--}365^\circ\text{C}$, regardless of whether this is the deposition or annealing temperature. Rutile films are initially observed on silicon substrates at deposition temperatures above 700°C , and more typically from 900 to 1100°C . It should be noted that anatase is a metastable phase of TiO_2 , and the

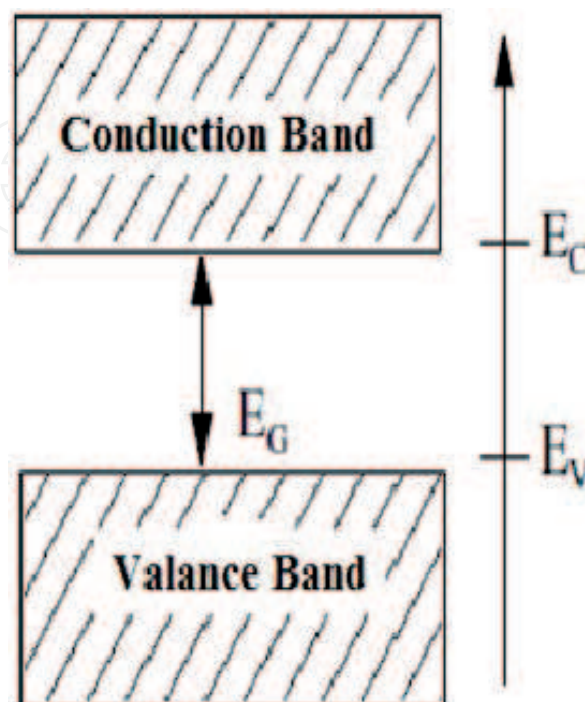


Figure 4.
 The band diagram of a semiconductor.

conversion to rutile involves a collapse of the anatase structure, which is irreversible [21, 22]. Although rutile and anatase are both of tetragonal crystallographic structure, rutile is more densely packed and thus possesses a greater density.

The deposition of TiO_2 thin films is formed by chemical reaction, using chemical vapor deposition (CVD), and spray pyrolysis and hydrolysis systems. In this scenario, the substrate temperature is the primary means of controlling the deposited phase of the material. In contrast, physical vapor deposition (PVD) systems, such as evaporation, sputtering, and ion-beam deposition, are used to determine the structure with its phase primarily by the kinetic energy of the impinging atoms.

Therefore, the progression through the amorphous, anatase and rutile phases may not necessarily be expected. This is confirmed by the occurrence of rutile films at low deposition temperatures ($< 450^\circ\text{C}$) by carefully optimized deposition methods, [23, 24] ion-assisted deposition [25] and reactive evaporation [26]. The TiO_2 films are formed by a chemical reaction, where the substrate temperature dominates film growth characteristics. Several researchers observed that the processing temperatures required to convert an anatase film into a rutile one are much higher than temperature required depositing a rutile film directly [26–28]. The variation in physical and chemical properties of the films is determined solely by the maximum processing temperature, whether the deposition temperature or a subsequent annealing temperature was observed by researchers [20].

The mechanism for the sintering and transformation of anatase into rutile involves several steps. Initially, the smallest particles coalesce, forming bigger particles. The fractions of particles that are already large have been shown not to undergo sintering. The heat evolved from the exothermic sintering process causes the local nucleation of the rutile phase. Finally, as the conversion to rutile is also an exothermic process, this results in the transformation of the whole particle to rutile.

4.2.2 The effect of impurities on the anatase-rutile phase transformation

In many research works, researchers have observed that the inclusion of a certain amount of impurities into TiO_2 can drastically alter the physical properties of the film. It has been shown that silicon and phosphorus inhibit the transformation from anatase to rutile, with 100% anatase phase being retained at temperatures as high as 870°C for up to 3 h for thin films 80 K and 1500 K for bulk samples [29]. The retardation of the anatase-rutile transformation can be achieved with impurities [29]. Most researchers agree that oxygen vacancies are responsible for the overall transformation mechanism [30]. Thus, the oxides and fluorides that assist the transformation can substitute for Ti^{+4} in the anatase lattice, resulting in the creation of oxygen vacancies. On the other hand, the inhibiting effect of other impurities involves the reduction of oxygen vacancies due its substitution into the anatase lattice.

Titanium alkoxides are common TiO_2 precursors, with the most frequently used being titanium tetra isopropoxide (TTIP) (also called tetra isopropyl titanate). The residue of the organic binders results in carbon contamination of typically a few atomic weight percentage (at. wt.%), but as high as 13 at. wt.% being observed [31]. It is likely that carbon incorporation could be higher at low growth temperatures, as when higher temperatures were used the carbonate species decomposed, resulting in the removal of hydrocarbon fragments [32]. Titanium tetrachloride (TiCl_4) is another common TiO_2 precursor, and this results in chlorine contamination of the deposited film.

5. Importance and applications of TiO_2 thin films

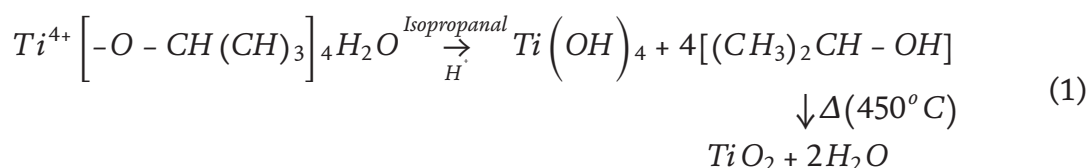
Due to its interesting intrinsic properties, TiO_2 thin films have great importance and significance for a large variety of industrial applications. Titanium oxide, which

belongs to the metal transition oxide family, was the most studied during the last two decades and demanded material in many fields of applications such as transparent electrodes, gas sensors, solar cells (PV), photocatalytic process, etc. To improve the performance of this oxide, doping TiO₂ with suitable metal ion dopants offers an effective method to adjust some of its physical properties. Generally, the doping of semiconductors with appropriate metallic element (Al, Nb, Sn, Ge, Fe, Ni and Cr) is one of the most effective ways in research for developing sensitivity applications such as photovoltaic solar cells, photocatalysis and pollution sensors. However, the interaction between the doping metals and the semiconductor is complicated because the interaction relates to the carrier concentration, defect level and surface states of the semiconductor, electronic, optical properties, and so on.

6. Synthesis of titania

The sol-gel technique is a suitable method for deriving nano-TiO₂ having unique metastable structure at low temperatures and excellent chemical homogeneity [33]. The novelty of the work is to synthesize nanosized (<25 nm) TiO₂ particles by optimized preparatory parameters associated with sol-gel method and characterize for their structural and optical behavior useful to photovoltaic application.

The synthesis process includes that the precursor TTIP, 3.5 mL, was slowly added to the mixture of isopropanol (25 mL), concentric hydrochloric acid (0.1 mL, catalyst) and distilled water (0.2 mL) with constant stirring for 30 min. The mixture undergoes hydrolysis reaction resulting in transparent pale yellowish solution. Then, the solution was allowed 24 h for gelation period. The gel was dried at 373 K for an hour and finely ground with mortar. Finally, the TiO₂ powder was calcinated at 673 K for an hour to obtain a nanosized particle with desired phase [34]. The different steps are involved in synthesis of nano-TiO₂ powder by sol-gel method and it was represented by the chemical reaction [35] in the system is



Characterization of TiO₂ powder was carried out by using X-ray diffraction analysis (**Figure 5**) with XPERT-PRO X-ray diffractometer in the range of 2θ values from 20° to 80° (λ = 0.1540 nm). The 7.7-nm-sized particles were determined from Debye-Scherrer's formula. The surface morphology of TiO₂ pellet (**Figure 6**) obtained using the VEGA3 TESCAN scanning electron microscope confirms nanosize spherical-shaped particles uniformly distributed without any aggregation and atomic force microscope AFM XE-100 topography images (**Figure 7**) exhibit the distribution of uniform spherical-shaped particles. The chemical compositions such as Ti (26.36 at. wt.%), O (68.5 at. wt.%) and C (5.07 at. wt.%) in the prepared TiO₂ powder were confirmed by the energy dispersive X-ray (EDX) spectroscopy (**Figure 8**). The absorption and transmission spectra were obtained using Perkin Elmer Lambda 35 UV/Vis Spectrophotometer and its transmittance is about 60% (**Figure 9**). The Fourier transform infrared (FTIR) spectra (**Figure 10**) were taken using SPECTRUM-RX 2 and represents the characteristic peaks in the range of wave numbers 4000–400 cm⁻¹.

The TiO₂ nanoparticles of size 7.7 nm have been prepared by optimized sol-gel technique. The XRD analysis reveals that the TiO₂ powder was highly crystalline (anatase phase) and nanostructured with tetragonal system. The SEM images exhibit the nanosized TiO₂ particles with less densification nature. The AFM

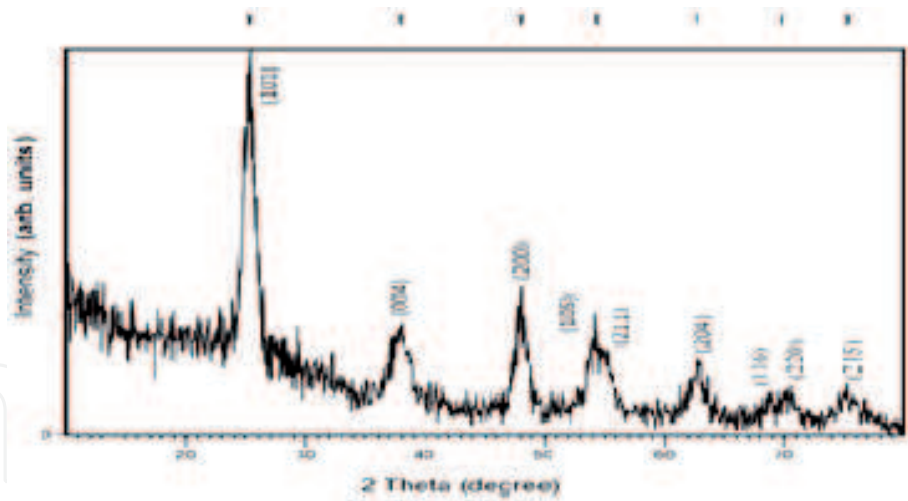


Figure 5.
X-ray diffraction pattern of TiO_2 powder calcined at 450°C .

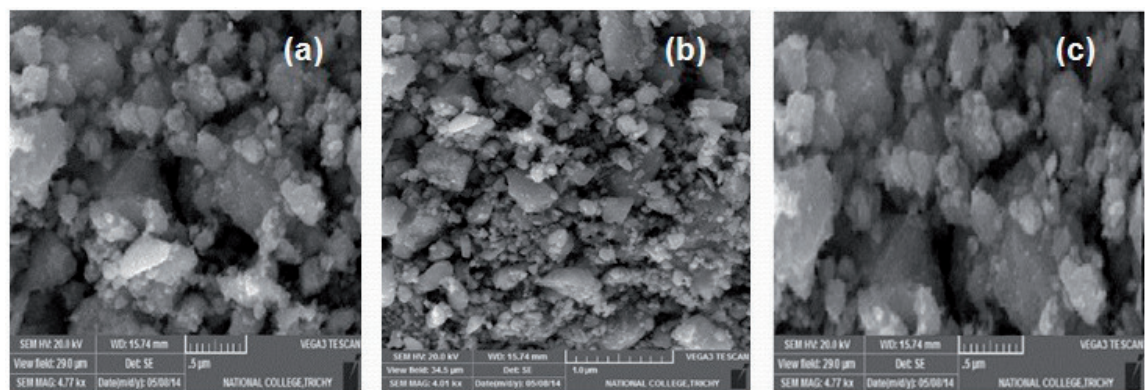


Figure 6.
SEM micrographs of TiO_2 powder (a) before (b) and (c) calcined at 450°C with different magnifications.

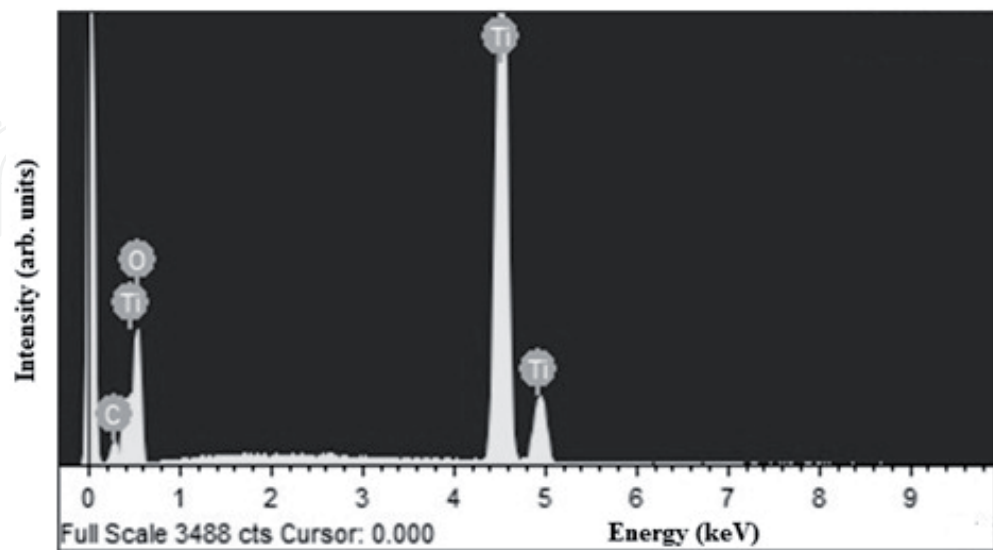


Figure 7.
EDAX spectra of TiO_2 powder calcined at 450°C .

study confirms the uniform distribution of spherical-shaped particles. The optical band gap of the TiO_2 is found to be 3.45 eV making it suitable for solar cell applications.

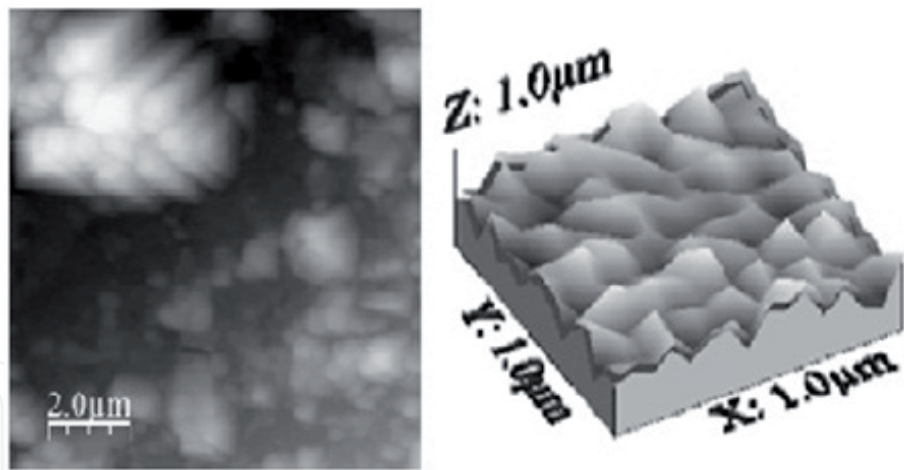


Figure 8.
AFM topographic images of TiO₂ powder calcined at 450°C.

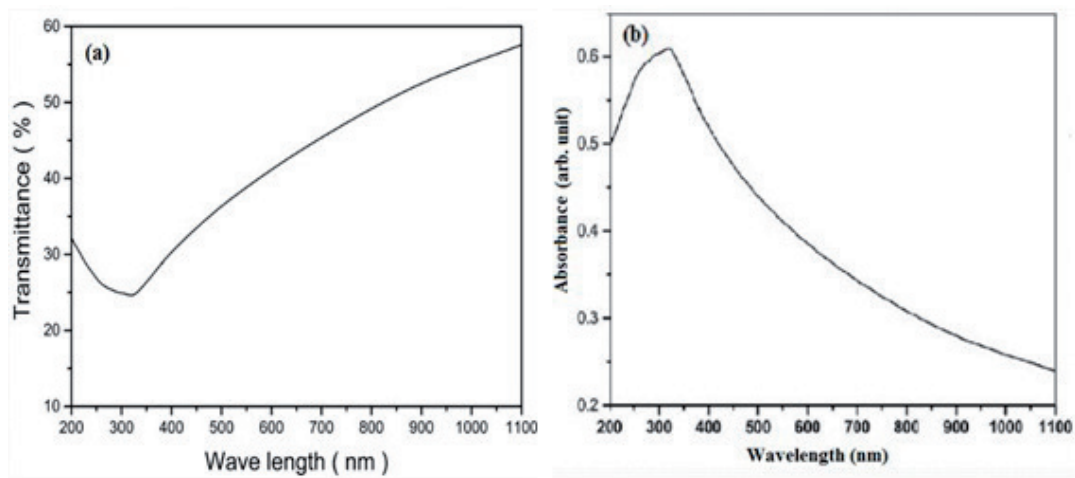


Figure 9.
UV (a) transmittance and (b) absorption spectra of TiO₂ powder calcined at 450°C.

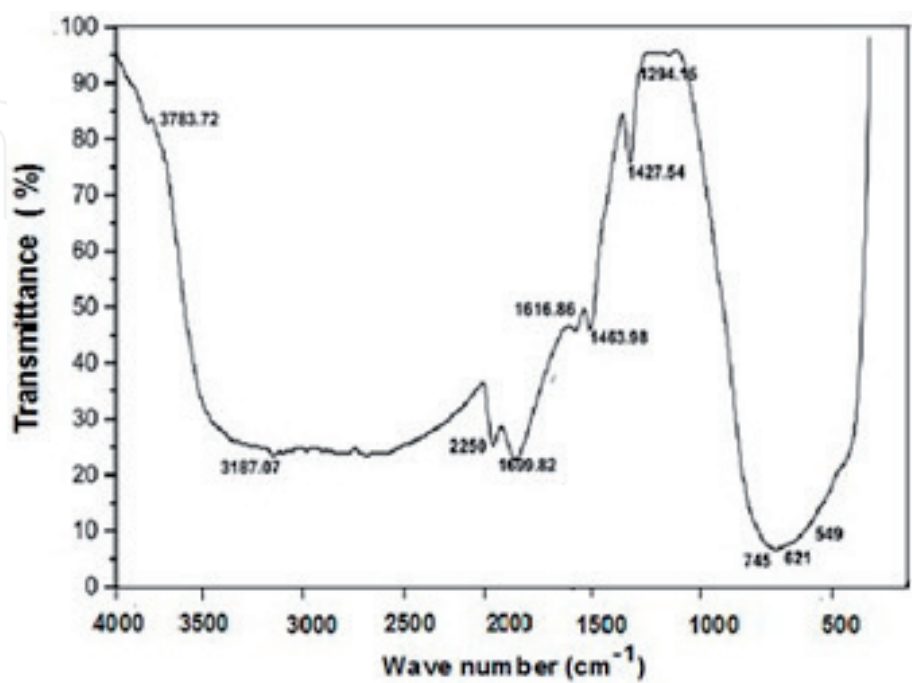


Figure 10.
The Fourier transform infrared (FTIR) spectra of TiO₂ powder calcined at 450°C.

7. Preparation of sol-gel routed nano-TiO₂ thin films and their effect of molarity

Nanocrystalline titanium dioxide (TiO₂) films are extensively studied because of their interesting chemical, electrical and optical properties. TiO₂ is one of the most important transition metal oxide semiconductors with wide band gap. A wide variety of techniques have been used to prepare titania films. Among these, the sol-gel routed spin coating technique has emerged as one of the most promising methods as it produces films by simple synthetic route with good homogeneity, low cost, excellent compositional control and feasibility of producing thin films on large complex shapes with low crystallization temperature.

This work is keeping the optimization of the processing parameters such as pH value (~8), amount of catalyst (HCl), spin speed (3000 rpm) and calcination temperature (450°C) constant to prepare nano-TiO₂ thin films with molar concentrations 0.05 M, 0.1 M, 0.15 M and 0.2 M by sol-gel routed spin coated technique. And also the study of the effect of molarity on structural, optical and electrical behaviors is useful to photovoltaic applications.

The titanium tetra isopropoxide (TTIP) was used as a precursor, hydrochloric acid as a chelating agent, isopropanol and deionized water as a solvent. Triton X-100 was used as a stabilizer to avoid precipitation in solution and at the same time used to increase the conductivity of films. TTIP (3.5 ml) was slowly added to the mixture of isopropanol (25 ml), concentric Hydrochloric acid (0.1 ml, catalyst) and distilled water (0.2 ml) with constant stirring for 30 min. Introduction of isopropanol prior to TTIP induces immediate precipitation due to highly reactive alkoxide, therefore Triton X-100 was added as a stabilizing agent for the hydrolysis reaction. The resultant alkoxide solution was kept at room temperature for hydrolysis reaction for 2 hours, resulting in a transparent pale yellowish TiO₂ sol. The hydrolysis and the poly condensation of titanium alkoxides proceeds according to the mechanism Eq. (1)). TiO₂ sol was deposited on to a glass substrate by a spin coating unit with spin rate at 3000 rpm for 60s

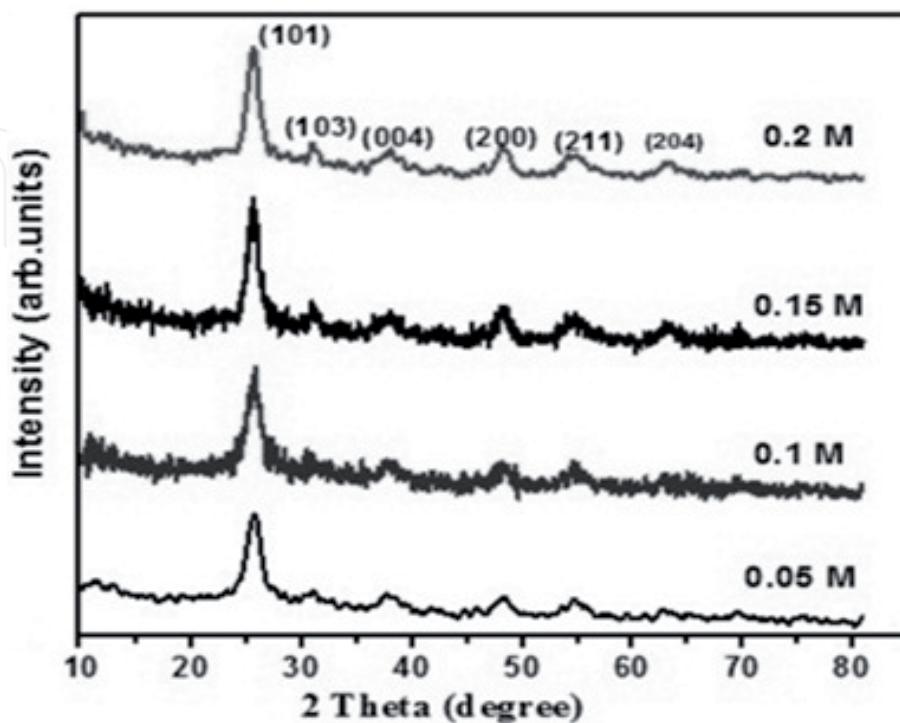


Figure 11.
X-ray diffraction pattern of TiO₂ thin films at different molar concentrations calcined at 450°C.

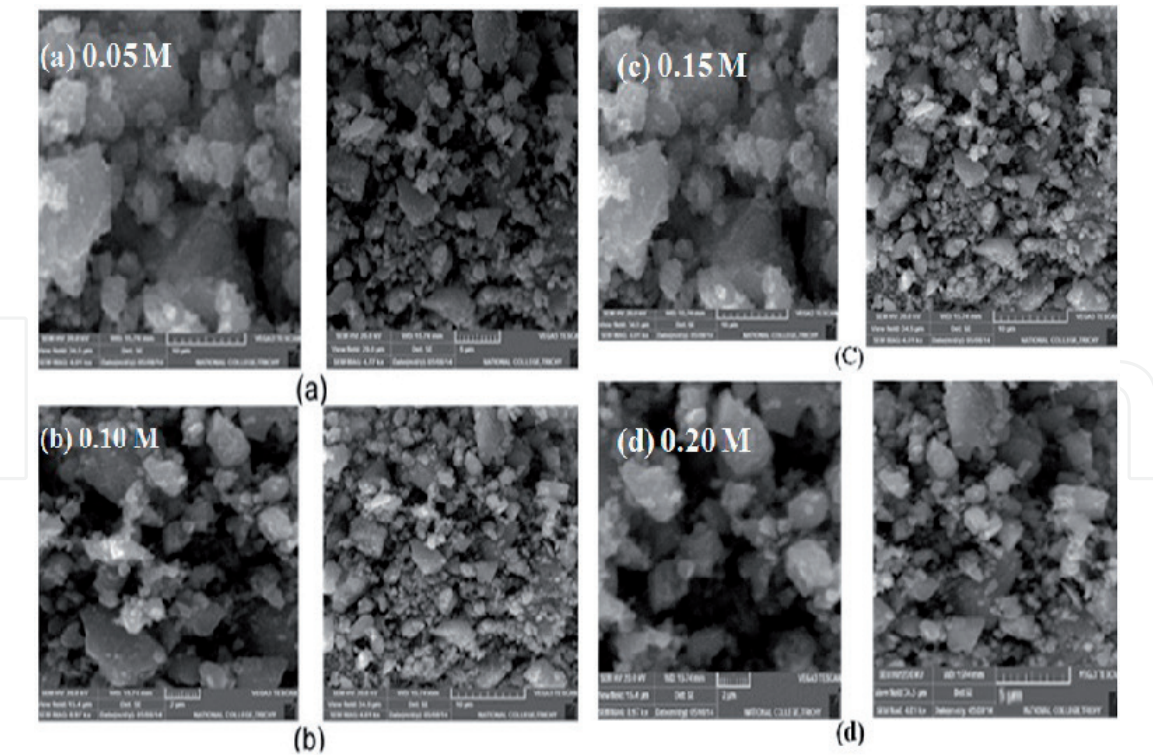


Figure 12.
SEM micrographs of doped and undoped TiO_2 thin films at different molar concentrations calcined at 450°C .

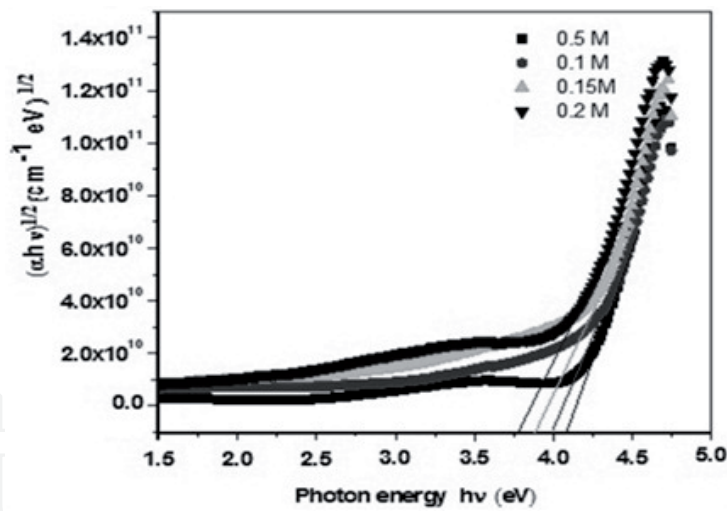


Figure 13.
Optical band gap energy of TiO_2 thin films at different molar concentrations calcined at 450°C .

in air and dried on a hot plate at 100°C for 60 seconds. The prepared samples were calcinated at 450°C for 1 hour [36].

The nanostructured titanium dioxide (TiO_2) thin films were prepared using the sol-gel routed spin coating technique. The X-ray diffraction pattern of TiO_2 thin films (**Figure 11**) exhibits that TiO_2 particles are crystallized as anatase phase and nanostructured with the tetragonal system. The SEM images (**Figure 12**) exhibit that the particles are spherical in nature. TiO_2 thin film prepared at 0.2 M concentration has a smooth surface. The roughness of the TiO_2 thin film increases with the increase of molarity. The optical transmittance is found to depend on the molarity and the higher value of molarity leads to lower optical band gap energy (**Figure 13**). Hence, the nano- TiO_2 thin films with higher molar concentration will be useful for photovoltaic applications due to their structural, optical and electrical behaviors.

8. Conclusions

Titanium dioxide (TiO_2) is one among the wide band gap metal oxide semiconducting materials used in thin films that have received much attraction due to its sensing properties, dielectric properties, antireflective coatings, good physical and chemical stability, high refractive index, low absorption, low cost, non-toxicity, high electron mobility, longer electron life time, low recombination losses and ease in preparation.

Titanium dioxide (TiO_2), also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium. Nanoscaled titanium dioxide (TiO_2) in thin layer or nanopowder forms appertains to the most extensively studied semiconductors. This metal oxide is a promising semiconductor frequently used due to its non-toxicity, chemical stability, photocatalytic activity and low cost [37, 38]. Especially, thin films as the nanostructured electrode materials have become very important in the fields of photovoltaics, energy storage, sensing, photo-electro-catalysis, etc.

TiO_2 in crystallographic form of anatase has become an interesting candidate as an n-type photoanode due to its band gap ($E_g = 3.2 \text{ eV}$), which is higher than that for the rutile phase ($E_g = 3.0 \text{ eV}$) and has excellent efficiency to generate the electron-hole pairs [39, 40]. The preparation of the nanostructured electrode materials with highly uniform nanoparticles has been investigated by many groups [41]. The most commonly used method is the sol-gel technique utilizing the molecular templates. The main advantage of this purely chemical method lies in a possibility of layer preparation under laboratory conditions as well as the possibility to tailor TiO_2 layer properties by varying preparation conditions. Nanoparticles with controlled chemical composition, size distribution, uniformity and dispersion can be readily synthesized using reverse micelles [42].

The TiO_2 thin films have been introduced as electron transport layers (ETL) because of their large band gap (3.7 eV) and well-matched energy levels (valence band of $\sim 8.1 \text{ eV}$ and conduction band of $\sim 4.4 \text{ eV}$). The requirements for ETL involve high electron mobility and transparency in the visible region to allow transmission of light into the active layer. These requirements limit the number of materials that have these characteristics, among which is the well-known and widely used titanium oxide [43].

Thus, in the present work, I have attempted to synthesis nanosized TiO_2 particles with 7.7 nm , which is less than commercially available TiO_2 powder (25 nm), and modified preparatory condition followed to prepare nanocrystalline TiO_2 thin films with different molar concentrations. The results from the above study exhibits that the prepared nano TiO_2 films with different molar concentrations are to enhance the optical, structural and electrical behavior of film which is suitable for photovoltaic applications.

Conflict of interest

The authors declare no conflict of interest.

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