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TiO_2 thin films: Impact of substrate temperature on structural and morphological properties

R. Suresh [a,*], S. Subash [a], K. Thirumal Valavan [a], M. Justin Paul [a],

T. Indira Priyadharshini [a]

[a] Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-641 020, Tamil Nadu, India.

*Corresponding author Email: rsdphy@gmail.com

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Abstract: Smooth and white spherical shaped TiO_2 thin films are successfully deposited by Nebulizer Spray Pyrolysis (NSP) technique. The TiO_2 thin films are characterized by XRD, SEM, DRS, PL and I-V analysis. Anatase phase polycrystalline tetragonal structure with preferential orientation along (1 0 1) direction obtained form XRD. The expansion and contraction of Ti-O bonds leads to a high crystalline nature with its purity at 289 nm. The absorbance increases with substrate temperature due to the decrease of film thickness, packing density and shrinkage of spray droplets. TiO_2 thin films indicate that the film is made up of small granules having slab like particles with some voids at lower temperature. The tiny particles are combined together to form white spherical shaped flower particles with pinholes at 450°C. A room temperature resistivity of the film deposited at 400°C is found to be in the order of 10^5 Ω/cm, which decreases to 10^3 Ω/cm for the films prepared at 450°C.

Keywords: TiO_2, Anatase, Tetragonal, DRS, NSP

1. Introduction

Titanium dioxide (TiO_2) has been one of the most attractive materials in the experimental investigation during the last decades due to its scientific and technological importance. For example, the electrochemical photolysis of water with TiO_2 was intensively studied as a candidate for a new energy source [1]. Sterilization and sewage disposal using TiO_2 as an electrochemical catalyst were also investigated. Among many processing techniques, the spray pyrolysis deposition (SPD) technique is one of the most promising ones, since the structure of the apparatus is quite simple and the technique is applicable to produce thin films on a large scale [2]. Titanium dioxide (TiO_2) is highly important in both theoretical and experimental field of research because of its very interesting electronics structures, which can be tuned by several processes. It has wide range of industrial and technological applications as pigment, photo catalyst and UV absorption. Hence, TiO_2 is an important compound suitable for fuel cells, solar cells, different sensors, pollution control system, waste management and self-cleaning glass coating materials along with food, cosmetic, paint, UV protectors etc [3-11].

Nontoxicity, chemical stability, poor solubility and high refractive index are properties which add to its practical applicability. Physical properties of TiO_2 not only depend on the phase structure but it depends also on the agglomerated micro structure, pores and particle size. For different physical and chemical process like charge transfer, chemical reaction, photon absorption etc. the molecules on the surface of a particles are more active than those stay inside [12-14].

2. Materials and methods

All reagents used in the synthesis were analytical grade and used without further purification. TiO_2 thin films were prepared through Nebulizer spray pyrolysis (NSP) method. In a typical process, 0.25 M of titanium isopropoxide was dissolved in 50 ml of deionized water and ultrasonicated for 10 minutes. The stirring is continued for 30 minutes to get clear and homogeneous spray solution. The nebulizer is connected to an air compressor. The prepared solution was sprayed onto ultrasonically cleaned glass substrates with different substrate temperature 400-

500°C. Films prepared by this method have smooth surface and well adherent with the substrate.

3.2 Result and Discussion

3.2.1 Optical properties

Absorbance spectra of the Titanium oxide thin films prepared with different substrate temperature is shown in Fig. 1. It increases up to a certain wavelength in UV region, then decreases exponentially and finally becomes constant in the visible region. It also shows a sharp and strong absorption edge in the wavelength 289 nm in the UV region. The prominent broad exciton absorption band was observed at 289 nm which support the formation of mono- dispersible colloidal particle due to quantum confinement effect. TiO_2 thin films would allow more light for absorption in UV region due to its rough surface whereas the same would allow moderate light absorption in visible region due to its high packing density. The expansion and contraction of Ti-O bonds leads to a high crystalline nature with its purity at 289 nm. The absorbance increases with substrate temperature due to the decrease of film thickness, packing density and shrinkage of spray droplets. The values of the tangents intercepting the energy axis give the values of optical band-gap as shown in Fig. 2. The calculated optical band-gap is found to be in the range 3.13 to 3.33 eV for indirect allowed transitions. The band-gap energy is decreases (3.33-3.13) with increasing substrate temperature mainly due the decrease of packing density and increase of crystallite size [15]. Diffuse reflectance spectra of TiO_2 thin films as shown in Fig. 3.

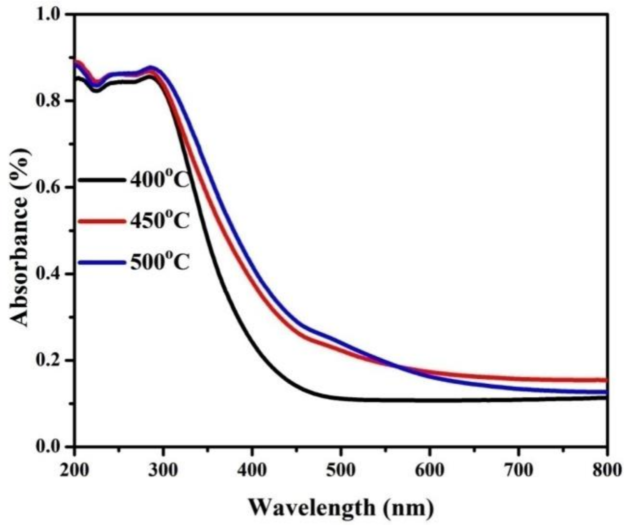

Figure 1 UV-Vis absorbance spectra of TiO_2 thin films.

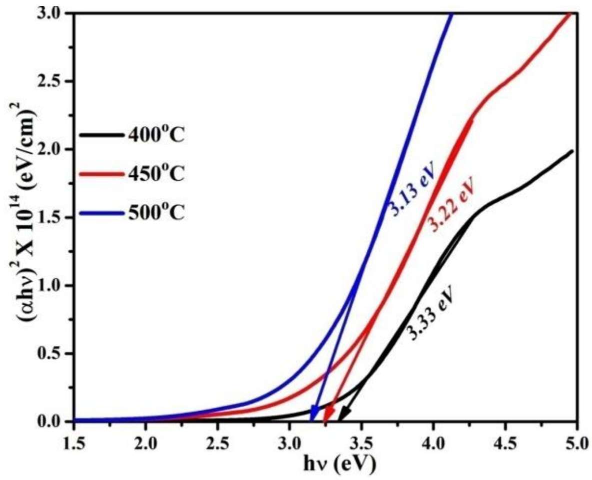

Figure 2 plot of Band-gap energy of TiO_2 thin films.

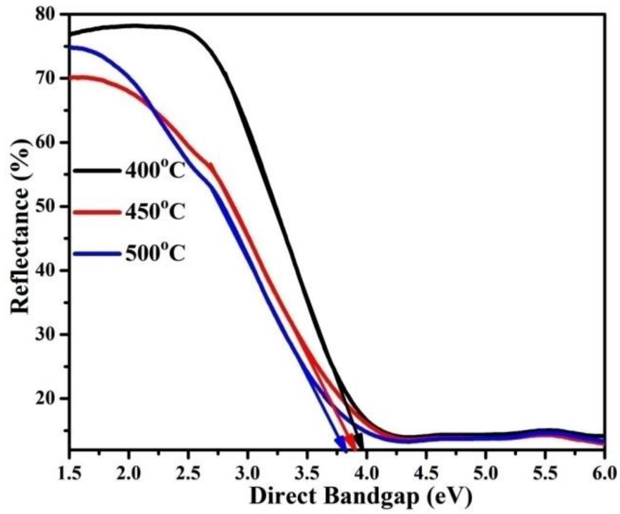

Figure 3 Diffuse reflectance spectra of TiO_2 thin films.

It decreases exponentially up to a certain wavelength in UV region and then finally becomes constant in the visible region. The direct allowed band-gap energy is in the range 3.83-3.97 eV.

3.2.2 Structural properties

The crystal phase and purity of the prepared TiO_2 thin films were identified using the powder X-ray diffraction (XRD) measurement. Fig. 4 shows the XRD pattern of TiO_2 thin films. These XRD pattern confirms the polycrystalline nature anatase phase tetragonal structure with preferred orientation along (101) direction i.e. normal to the plane of particle surface. The observed peak positions are in good consistency with JCPDS card No. 89-4203. The XRD pattern consists of six Bragg peaks are observed at 2θ = 25.05, 37.72, 47.98, 53.75, 54.91 and 62.47° which corresponds to crystal the planes of (101), (004), (200), (105), (211) and (204) respectively [16]. The diffraction peaks in the XRD pattern are very narrow and sharp, which represents the samples thus prepared are good crystalline materials (indicates the good crystallinity of the TiO_2 samples). Influence of substrate temperature strongly induce the growth of peak which indicates the increased intensity of (101) peak. The substrate temperature strongly distresses the growth of doublet peaks (105) and (211) whereas the same augment the growth of (004) and (200). The reason for comparatively lower peak intensities at lower temperature (500°C) is due to low packing density and incomplete growth of the film. As the substrate temperature increases, the crystallinity of the films increases up to 450°C. Further increase in substrate temperature decrease the peak intensity and it is attributed to the shrinkage of spray droplets, which reduce the thickness of the films [17]. The crystallite size of the SrO samples is calculated using Scherer formula and it is found to be in the range 17.4-46.2 nm. The increase in crystallite size is may be owing to change in nucleation process caused by induced stress due to the presence of heat treatment which leads to coalescence of islands to form bigger crystallites.

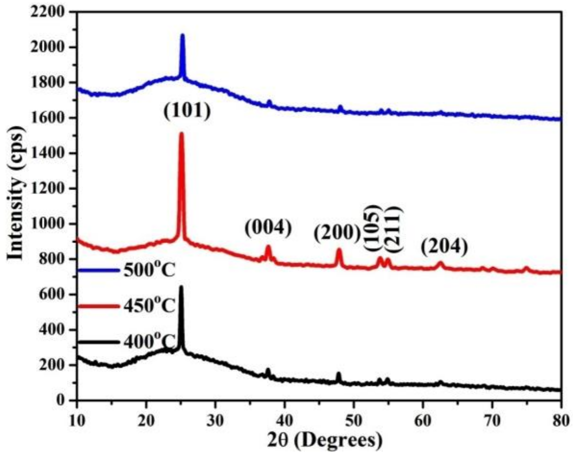

Figure 4 XRD patterns of TiO_2 thin films.

3.2.3 Photoluminescence properties

Fig. 5 shows the PL spectra of TiO_2 thin films. Three consistent sharp and broad peaks are observed at 290 (3.87 eV), 386 (3.64 eV) and 465 (2.65 eV) correspond to Near Band Emission (NBE) at UV region and Deep Level Emission (DLE) at violet and green emission in the visible region respectively. The emission peak obtained at 386 nm could be related to the hopping of electrons from the localized Ti3d state to the O2p valence band. The broad peak observed at 290 nm could be due to band edge excitonic emission. The emission peaks at larger wavelength 465 nm are attributed to the quasi-free recombination at the absorption band edge [18]. The oxygen vacancies and adsorbed surface hydroxyl groups (due to moisture adsorbed because of sample handling and exposing to the environment prior to measurement) are dominant sites for trapped electrons and holes. These trapped carriers, which are captured by oxygen vacancies and surface hydroxyl groups.

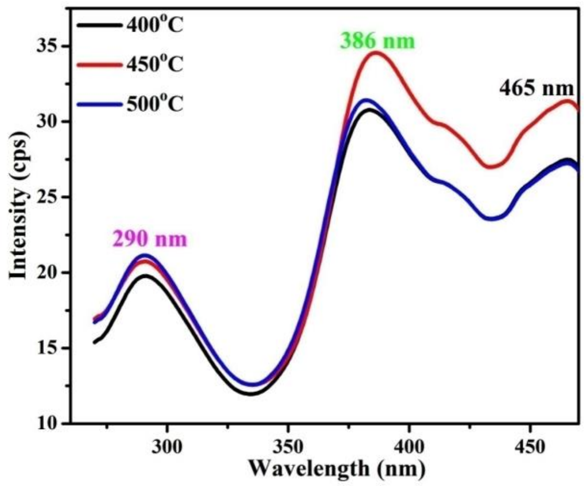

Figure 5 PL spectra of TiO_2 thin films.

3.2.4 Morphological properties

Fig. 6 depicts the SEM images of TiO_2 thin films prepared with different substrate temperature by NSP method. TiO_2 thin films indicate that the film is made up of small granules having slab like particles with some voids at lower temperature. The tiny particles are combined together to form white spherical shaped flower particles with pinholes at 450°C. It also reveals the presence of tiny dust granules with rough surface at higher temperature [19]. These results indicates that the substrate temperature slightly amend the morphological observations.

3.2.5 Electrical properties

I-V characteristics of TiO_2 thin films is represented in Fig, 7. It exhibits nearly linear response to the applied voltage at high temperature. At low temperature, conductivity increases slowly with temperature whereas the same increases rapidly at high temperature. The calculated electrical conductivity is found to be varied in the range 6.49×10^{-5} to 1.89×10^{-3} S/cm for different temperature 30-120°C. A room temperature resistivity of the film deposited at 400°C is found to be in the order of 10^5 Ω/cm, which decreases to 10^3 Ω/cm for the films prepared at 450°C. The activation energy decreases with the increase of substrate temperature from 1.125 to 0.649 eV due to the presence of numerous pinholes appeared in the films obtained from SEM images and improved crystallinity.

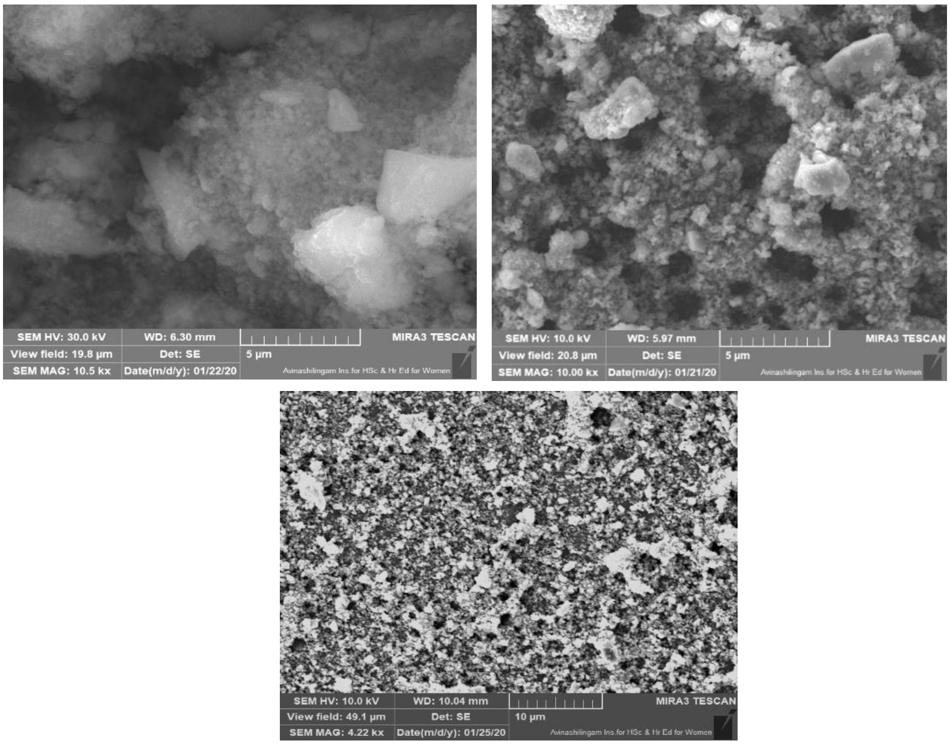

Figure 6 SEM images of TiO_2 thin films

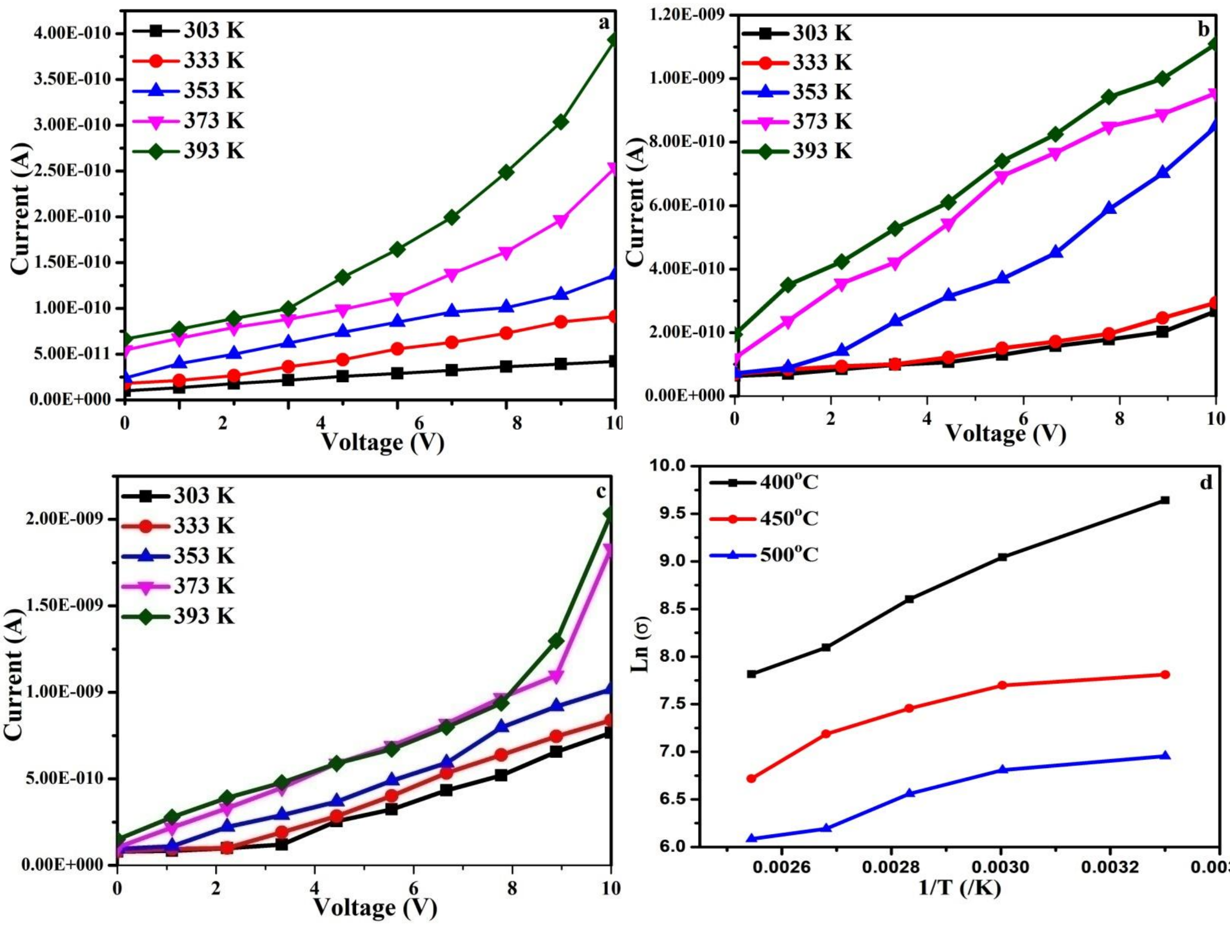

Figure 7 I-V characteristics of TiO_2 thin films

4. Conclusion

Substrate temperature strongly influences the optical & structural parameters, morphological changes and electrical properties in the following aspects,

- XRD patterns exhibit the presence of anatase phase tetragonal structure with dominant orientation along (101) direction without any lattice disorder and impurity phase.
- Three consistent sharp and broad peaks are observed from emission spectra at 290 (3.87 eV), 386 (3.64 eV) and 465 (2.65 eV) correspond to near band edge emission (NBE) at UV region, deep level emission (DLE) at violet and green in the visible region respectively.
- The band-gap energy is decreases (3.33-3.13 eV) with increasing substrate temperature mainly due the decrease of packing density and increase of crystallite size.
- SEM images reveal the existence of slap, spherical and small dust granules particles with pinholes and voids.
- The calculated electrical conductivity is found to be varied in the range 6.49×10^{-5} to 1.89×10^{-3} S/cm for different temperature 30-120°C.
- The activation energy decreases with the increase of substrate temperature from 1.125 to 0.649 eV due to the presence of numerous pinholes appeared in the films obtained from SEM images and improved crystallinity.

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Authors Contribution

Conceptualization, methodology, manuscript preparation, review and editing (RS). Manuscript Review and Editing (SS, KTV, MJP & TIP). All the authors have read and approved the manuscript.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Ethics Approval

Ethics approval doesn't required for this study

Conflict of interest

The authors have no conflicts of interest to declare that they are relevant to the content of this article.

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