Synthesis and Characterization of TiO_2 Thin Film by Silar Method

Shukri Rashed M. Hussein, Vishnu Kutwade and Ramphal Sharma
Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad431004, India.

Abstract - In this study, SILAR method is adopted for the deposition of titanium dioxide (TiO_2) thin films were used. Titanium trichloride ($TiCl_3$) and ammonium hydroxide are used as the cationic and anionic precursors respectively. Deposition parameters such as individual dipping, growth rate, rinsing times, and precursor concentration are optimized to obtain a uniform, adherent films. The as-deposited films are annealed at 400 °C for one hour. The crystal structure of the films are analyzed by X-ray diffraction. Effect of deposition parameters on the optical properties of the films is analyzed UV-Vis spectrophotometry. Fourier-transform infrared spectroscopy (FTIR) was used to determine functional groups. The optical properties and determination of the energy gap value were studied using the UV- visible spectrum so that the energy gap value was 3.32 ev.
Keywords: TiO_2, Thin film, SILAR, X-ray diffraction, UV-Vis, FTIR, Band gap.

I. INTRODUCTION

The TiO_2 nanoparticles are of interest due to their unique technological properties and applications such as sensors, memory devices, solar cells, and photocatalysis [1,2]. Titanium dioxide is of very high technical importance due to its excellent electrical, optical, and chemical properties such as no toxicity, transparency in visible light, wide gap energy, high refractive index, electrochemical stability, and good insulation properties. [3]. Titanium

dioxide (TiO2) is a fairly transparent and wide-gap semiconductor that is considered one of the most common and excellent materials applied in photovoltaic devices as the electron transfer layer (ETL) [4]. For the synthesis of TiO2 films most of the known thin film production methods have been applied using various methods such as the sol-gel process, [5], electro deposition [6,7], chemical bath deposition and its modified version, the SILAR (Successive Ionic Layer Adsorption and Reaction) method [8,9]. SILAR is based on submerging the substrate in separately placed cations followed by rinsing after each reaction, allowing a heterogeneous reaction between the ions dissolved in the solution and the solid phase. The SILAR method is an ideal method for creating uniform, crystalline and compact films. Due to its simplicity. When compared to other technologies, SILAR offers a large number of advantages: SILAR does not require a vacuum and does not require a target throughout the process phases; by changing the number of sedimentation cycles, the film thickness and the deposition rate can be controlled over a wide range of sizes; This method is a very easy way to promote movies. It is considered very convenient in the case of large area sedimentation although there are no restrictions on the dimensions of the substrate [10]. There are several thin film deposition methods but the series ionic layer absorption and reaction (SILAR) method is relatively simple and offers a wide range of advantages over other expensive methods of thin film deposition [11-14] such as:

Through this process, the film thickness and deposition rate can be easily controlled over a wide range by changing the deposition cycles. It is a process by which relatively uniform films can be obtained on substrates of any shape, and there are no restrictions on substrate material, surface profile, or dimensions. Unlike the vacuum-based sedimentation method, the SILAR method does not require any complicated and expensive tools and also vacuum at anystage which is a great advantage in the context of industrial application. The operating temperature which requires the SILAR method is usually low. Apart from the obvious advantages in terms of energy saving, the lower sedimentation temperature avoids the effects of higher temperatures involved in various processes such as contamination, diffusion, and doping redistribution.

The aim of this study is to produce a tio2 film on a glass slide using the bunker method, to study some of its properties, and to study the nature of the resulting film. Solar cell application.

II. EXPERIMENTAL DETAILS

2.1 Materials Used

Titanium trichloride ($TiCl_3$) 15%, Sodium bicarbonate, ammonia solution 28% were procured from SDFCL, India. Microslides size 75mm x 25mm, thickness 1.35mm were purchased from ASGI, India. AR grade solvents such as ethanol and acetonitrile were used. Milli Q water (distilled water) was used.

2.2 Methods of Characterization of Synthesized TiO_2 Nanoparticles

The X-ray diffraction patterns were measured using Bruker D8 Advanced system, witha potential difference of 40 kV and a current of 40 mA with source Cu Ka $\lambda = 1.5406$ A radiation.

FTIR of absorption measurements were carried out using Alpha II, from BRUKER, wave number range 4000 cm-1 to 500 cm-1, spectral resolution 2$cm^{-1}$and. UV-Vis Spectrophotometer (Perkin Elmer, LAMDA 25) recorded the optical absorption spectra in the wavelength range 300–800 nm

2.3 Synthesis of TiO_2 Nanoparticles

In order to obtain TiO_2 thin films by the SILAR method, glass substrates were used. Which must be cleaned first with ethanol for a period of five minutes, then with distilled water, then acetone, then placed in the ultrasonic device for a quarter of an hour, then put in distilled water and finally dried in dry air.

25 ml of distilled water mixture in 5 ml of $TiCl_3$.1M of Sodium bicarbonate is added to the solution to control the value of the PH. This solutions as the source of the cation It is mixed for a few minutes until at room temperature for obtaining a homogenous solution. In thesecond baker 40 ml of deionized water.

In the third baker Ammonia is slowly added to distilled water until it becomes the value of PH is 12 as an anion source and stirred for a while maintaining the solution temperature continuously between (70-80) degrees Celsius. A fourth baker contains 40 ml of deionized water. First, glass substrates into the first baker, which includes the cation source, for 15 seconds, then put it in the second baker for 15 seconds. Deionized water is used for rinsing the substrate after immersion in the precursors which facilitates the removal of excess cations or anions which are loosely adsorbed onto the substrates figure 1.

The third step submerges the substrate in the baker, which includes the anion source for 15 seconds. Finally, dip into the fourth baker, which contains distilled water for 15 seconds. In this study, and for a good film thickness of the number of courses cycle 130.Each cycle consisted of the immersion of the substrates in each solution during 15second.The as- deposited films are annealed at 400 C^{o} for one hour. The crystal structure of the films is analyzed by X-ray diffraction.

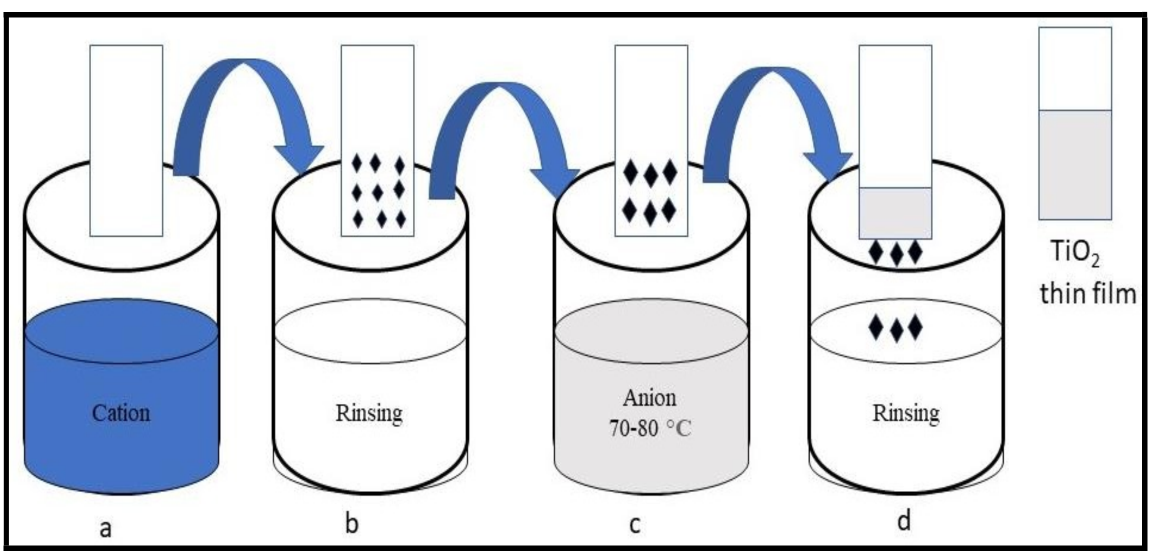

Figure 1: Silar method

III. RESULTS AND DISCUSSION

3.1 Characterization of TiO_2 nanoparticle

3.1.1 X-ray diffraction patterns

The X-ray diffraction analysis (XRD) pattern of the TiO2 thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα (λ=0.154 nm)) radiation, with a diffraction angle between 20° and 70°. The crystallite size was determined from the broadenings of corresponding X-ray spectrum peaks the phase composition and the structure of the film were studied by X-ray diffraction analysis. The XRD patterns ofTiO2 thin films are shown in Fig.1. The strong and sharp diffraction peaks indicate the formation of well crystallized TiO_2 thin films. The diffraction pattern shows a peak (101) plane of the anatase phase of TiO_2. The observed peaks correspond to (101), (004), (2 0 0), (1 0 5), and (2 13) planes. No peaks corresponding to the rutile or brookite phase were observed in the X-ray diffraction pattern figure 2

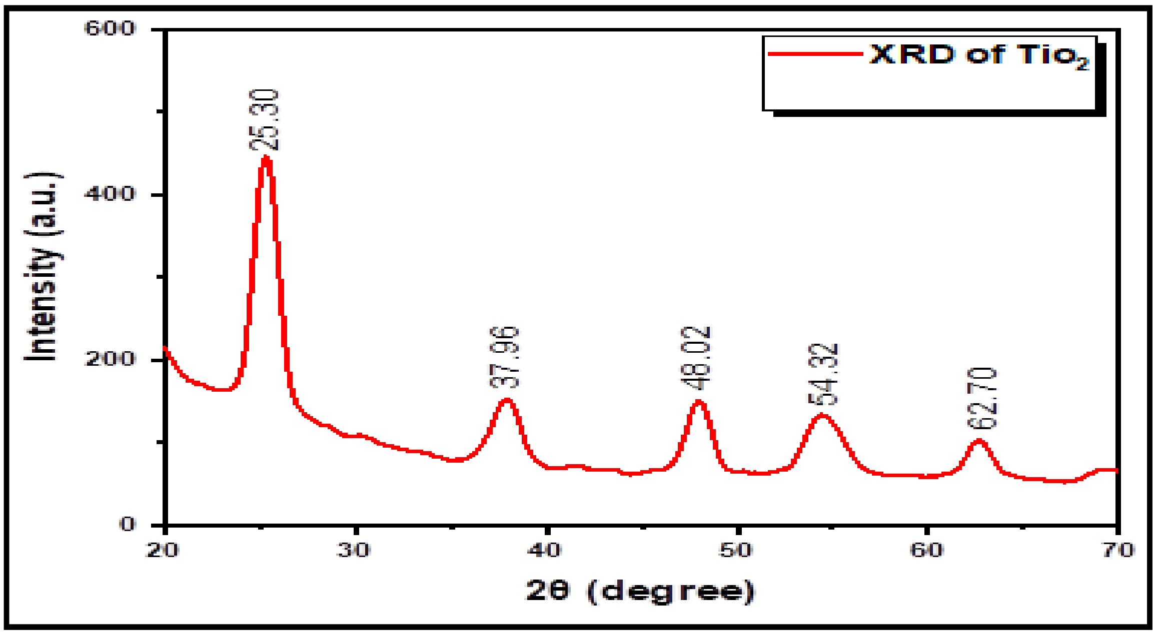

Figure 2: X-ray diffraction pattern of TiO_2

3.1.2 UV-V is absorption spectra of TiO2 film

The optical properties of TiO_2 films were studied using the absorption spectrum recorded with the help of a UV-Vis spectrophotometer. The optical absorption spectrum of the TiO_2 films was recorded in the range of 300-800 nm. The absorption spectrum of TiO_2 thin films is shown in figure 3a. A significant decrease in the wavelength can be ascribed to the absorption of light caused by the excitation of electrons from the valence bandto the conduction band of titania. It was observed that the optical absorption decreased smoothly from the UV to near IR region.

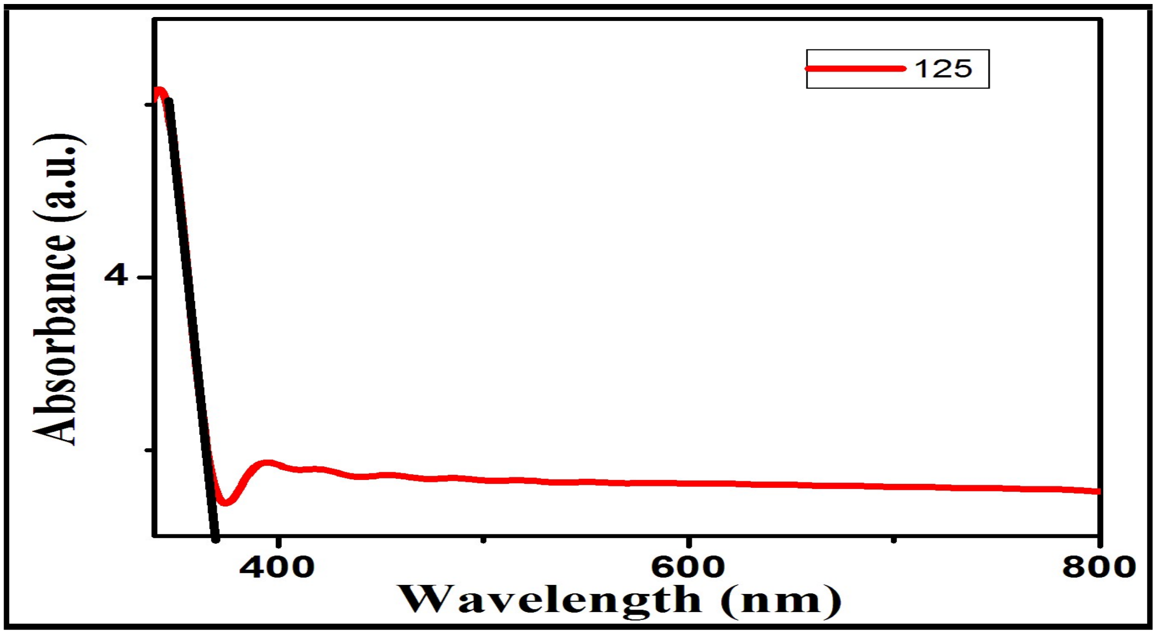

Figure 3a: Absorption spectra for TiO_2 thin film after annealed at 300 C° for 1 hr.

A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in figure 3bEg was evaluated using the extrapolation of the linear part. Using Tauc's plot, the energy gap (Eg) was calculated to be 3.32 eV.

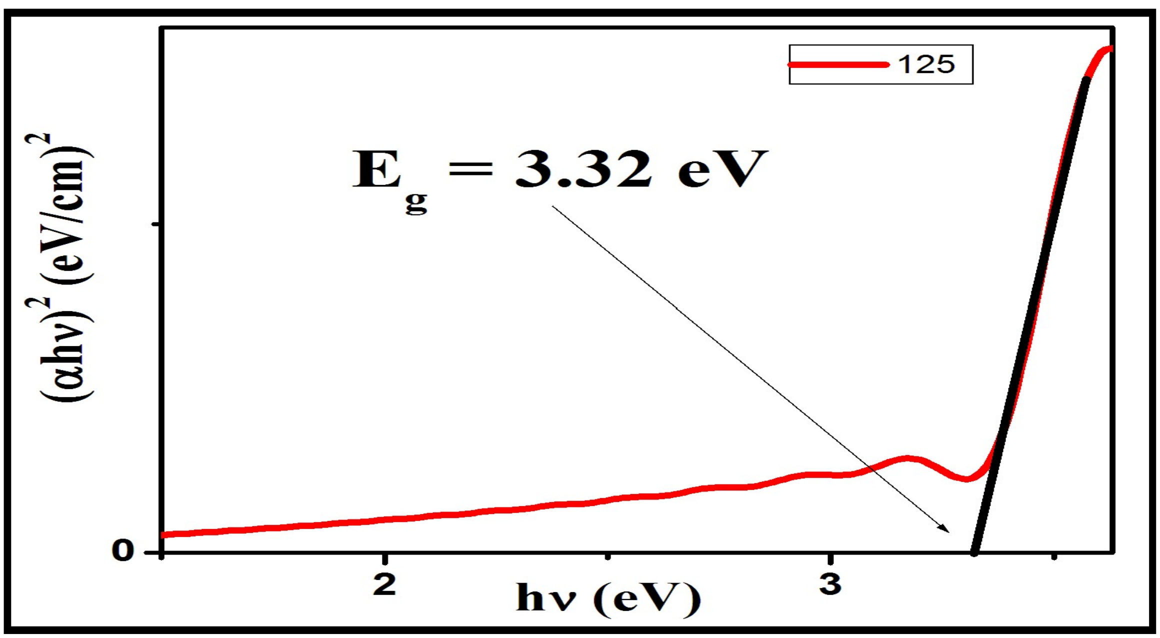

Figure 3b: Band gab of TiO_2 thin film.

3.1.3 FTIR Analysis

Fourier Transform Infrared (FTIR) spectroscopy is a potential method for observing molecular vibrations. The FTIR spectrum of the TiO_2 thin films are shown in figure 4. shows the FTIR spectra of TiO_2 nanostructures in the range 400-4000 cm–1. It shows the band at 3200-3550 cm–1 corresponding to the stretching vibration of the O–H group. It indicates the existence of water on the surface of TiO_2 nanowires. The C=O stretching mode of vibration is observed at 1540 cm^{-1} is assigned to the stretching vibrations of titanium molecules.

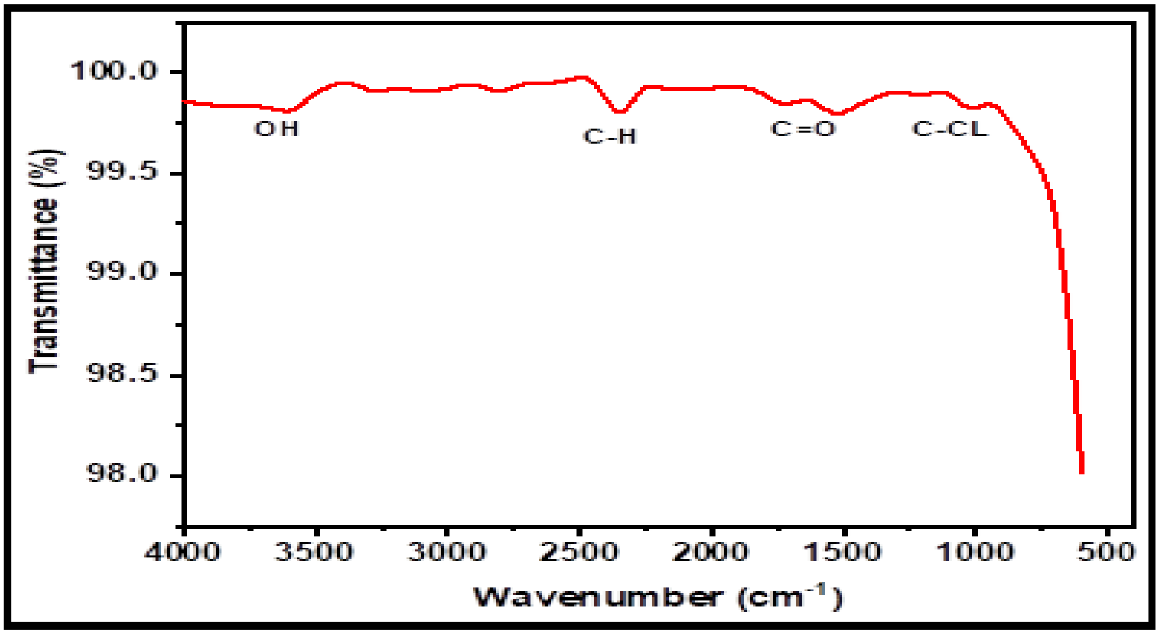

Figure 4: FTIR Analysis for TiO_2 thin films

IV.CONCLUSION

Thin films of titanium dioxide (TiO_2) are prepared by SILAR method at optimized deposition conditions. Annealing of the films at 400°C improved the crystallinity of the films. The effect of growth rate, adsorption/reaction time and cationic precursor concentration on the optical properties of the films is studied. The calculated direct band gap of the films is in the of 3.2 ev. The X-ray diffraction of the resulting film matched the reference values for TiO_2.This study showed that film thickness can be controlled through

the number of dipping cycles. The thickness of the resulting film was calculated in this studyand found to be within 100 nm.

REFERENCES

[1] Li, W., Shah, S. I., Huang, C. P., Jung, O., & Ni, C. (2002). Metallorganic chemical vapor deposition and characterization of TiO2 nanoparticles. *Materials Science and Engineering: B*, *96*(3), 247-253.

[2] Traversa, E. (1995). Design of ceramic materials for chemical sensors with novel properties. *Journal of the American Ceramic Society*, *78*(10), 2625-2632.

[3] Diebold, U. (2003). The surface science of titanium dioxide. *Surface science reports*, *48*(5-8), 53-229.

[4] Zhao, L., Jiang, Q., & Lian, J. (2008). Visible-light photocatalytic activity of nitrogen- doped TiO2 thin film prepared by pulsed laser deposition. *Applied Surface Science*,*254*(15), 4620-4625.

[5] Espinosa, R., Zumeta, I., Santana, J. L., Martınz-Luzardo, F., González, B., Docteur, S., & Vigil, E. (2005). Nanocrystalline TiO2 photosensitized with natural polymers with enhanced efficiency from 400 to 600 nm. *Solar Energy Materials and Solar Cells*, *85*(3), 359-369.

[6] Wang, Z., Helmersson, U., &Käll, P. O. (2002). Optical properties of anatase TiO2 thin films prepared by aqueous sol–gel process at low temperature. *Thin Solid Films*, *405*(1- 2), 50-54.

[7] Lokhande, C. D., Park, B. O., Park, H. S., Jung, K. D., &Joo, O. S. (2005). Electrodeposition of TiO2 and RuO2 thin films for morphology-dependent applications. *Ultramicroscopy*, *105*(1-4), 267-274

[8] Abdullah, H., Amalina, A., &Shaari, S. (2010). Study the morphology of tio2 thin films prepared by chemical bath deposition. *Solid State Science and Technology*, *18*(1), 150- 154.

[9] Patil, U. M., Gurav, K. V., Joo, O. S., &Lokhande, C. D. (2009). Synthesis of photosensitive nanograined TiO2 thin films by SILAR

method. *Journal of Alloys and Compounds*, *478*(1-2), 711-715.
[10] Jiménez-García, F. N., Segura-Giraldo, B., Restrepo-Parra, E., & López-López, G. A. (2015). Synthesis of TiO2 thin films by the SILAR method and study of the influenceof annealing on its structural, morphological and optical properties. *Ingeniare. Revistachilena de ingeniería*, *23*(4), 622-629.
[11] Pathan, H. M., &Lokhande, C. D. (2004). Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method. *Bulletin of Materials Science*, *27*(2), 85-111.
[12] Nicolau, Y. F., Dupuy, M., & Brunel, M. (1990). ZnS, CdS, and Zn1− x Cd x S thin films deposited by the successive ionic layer adsorption and reaction process. *Journal ofthe Electrochemical Society*, *137*(9), 2915-2924.
[13] Shinde, S. K., Ghodake, G. S., Fulari, V. J., & Kim, D. Y. (2017). High electrochemicalperformance of nanoflakes like CuO electrode by successive ionic layer adsorption and reaction (SILAR) method. *Journal of industrial and engineering chemistry*, *52*, 12-17.
[14] Kwon, C. H., Kim, J. H., Jung, I. S., Shin, H., & Yoon, K. H. (2003). Preparation and characterization of TiO2–SiO2 nano-composite thin films. *Ceramics International*, *29*(8), 851-856