ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis and Structural Studies on TiO_2 Thin Films

M. Seshu Kumar[1], M.P.D. Parimala[1], K. Ravindranadh[2] and M.C. Rao[1*]

[1]Research Scholar, Krishna University, Department of Physics, Andhra Loyola College, Vijayawada-520 008, India
[2]Physics Division, Department of Basic Sciences & Humanities, Chirala Engineering College, Chirala-523 157, India
[1]Department of Physics, Andhra Loyola College, Vijayawada-520 008, India

ABSTRACT

Transparent conductive oxides based semiconductor materials plays a crucial role in the development of thin film solar cells. Titanium dioxide has attracted researchers because of the many interesting physical and chemical properties that make it suitable for a variety of applications. TiO_2 exists in three crystalline phases; brookite, anatase and rutile. TiO_2 thin films have various technical applications in solar energy conversion, flatpanel displays, electrochromic devices, invisible security circuits, LEDs, etc. In the present investigation, TiO_2 thin films were prepared by sol-gel method. X-ray diffraction studies revealed the crystal system is indexed to be anatase crystalline state. The calculated average crystallite size of prepared samples was found to be 38 nm. SEM showed irregular shaped particle size clusters. EDS confirms the presence of constituent elements of prepared material. The characteristic vibrational modes of constituent elements in the host lattice were evidenced by FT-IR studies.

Keywords: TiO_2, Sol-gel, XRD, SEM and FTIR.

Corresponding author

INTRODUCTION

The current research and development activities are aimed at functional nanotechnology. The nanostructures are used to produce optical electronics or magnetic properties. Titanium dioxide is represented with chemical formula TiO_2. It has a wide range of applications. TiO_2 has attracted significant attention because of the many interesting properties which make it suitable for a different variety of applications. TiO_2 exists in three crystalline phases; brookite (orthorhombic), anatase (tetragonal with and rutile (tetragonal) [1, 2]. It is transparent in the visible range and has a wide optical bandgap [3-6]. This makes TiO_2 an excellent candidate for optical coatings [7-9]. It is also used for gas sensing [10]. TiO2 coatings with high photoactivity are attractive for industrial applications such as water and air purification by photocatalysis [11, 12].

For many applications anatase phase is favoured. Rutile TiO_2 is commonly used in the paint industry as a white pigment in paints. In order to prepare TiO_2 fine powders and films, a wide range of techniques have been used such as hydrothermal methods [13], electron beam evaporation [3], DC and RF magnetron sputtering [8] and sol–gel methods [11, 12]. Among these techniques the sol–gel method offers several advantages: fine powders and films with high homogeneity can be prepared using simple equipment, the thickness and the porosity of the films can be easily controlled by changing the concentration of the sol and large surface areas can be coated by spin or dip coating.

Titanium dioxide thin films have also many applications such as photocatalytic activity [14, 15]. TiO_2 has several advantages like a stable chemical property, no toxicity for organisms, no photo-corroding and higher bandgap energy (3.2 eV). TiO_2 has been studied widely for its numerous applications from optoelectronics to cosmetics [16]. It has excellent photocatalytic oxidative properties [17]. TiO_2 has been used in water and air pollution treatments [18]. It also utilized in various technological applications such as humidity sensor, gas sensor and membrane [19].

In the present study, sol-gel process is proposed because it is a convenient and versatile method for preparing transparent thin film at low temperature. The properties depend on the precursor solution [20]. Sol-gel process is very convenient to deposit transparent materials in combination with spin coating technique. Rao et al. have presented the results on different oxide materials in their earlier studies [21-30]. In the present investigations, TiO_2 thin films were prepared by sol-gel method and characterized by XRD, SEM with EDS, TEM FT-IR.

EXPERIMENTAL

Thin films of titanium oxide were prepared using sol–gel technique. Titanium IV isopropoxide $(Ti(OCH(CH_3)_2)_4$ as precursor and isopropyl alcohol$(CH_3)_2CHOH$ as solvent were used to synthesize the sols. Glacial acetic acid was used in order to begin hydrolysis via an esterification reaction. To prepare a stable precursor solution, first $(Ti(OCH(CH_3)_2)_4$ and $(CH_3)_2CHOH$ were mixed. The molar ratio of 1.3 was maintained between $(Ti(OCH(CH_3)_2)_4$ and $(CH_3)_2CHOH$. This mixture was stirred for 30 min at room temperature. Acetic acid was slowly added into the alkoxide solution under stirring for 30 min at room temperature. A molar ratio of 1:3 was utilized between acetic acid and $(Ti(OCH(CH_3)_2)_4$. A white precipitate is formed. Finally Methanol (1:8) was added to get a moonstone color precipitate. Let this precipitate settle for 60 min. A soda lime glass (SLG) was dipped in this sol and remain for 30 min and one more SLG for 60 min. Both the SLG's are annealed at 500 ^{0}C.

X-ray diffraction patterns were recorded on PANalytical Xpert Pro diffractometer with CuK_α radiation. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images are taken on ZEISS EVO 18. Transmission electron microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing samples in ethanol. Bruker FT-IR spectrophotometer is used for recording FT-IR spectrum of the prepared samples in the region 400-4000 cm^{-1}.

RESULTS AND DISCUSSION

XRD Studies

TiO_2 exhibits anatase crystalline state. XRD spectra of the prepared TiO_2 thin films were shown in Figure-1. These prepared thin films are with a preferred orientation of (101), (004) and (211) peaks which confirms the anatase crystalline state. XRD pattern of this optimized sample is in good agreement with the reference pattern of TiO_2 with standard diffraction data of JCPDS file No.21-1272 [31]. The average crystallite size of the sample is calculated from the full width at half maximum intensity of the XRD peaks using Debye - Scherrer's formula,

$$D = (K \lambda / \beta \cos\theta)$$

where

D is the mean crystallite size,
K = 0.9 is Scherrer's constant,
λ is the wavelength of the incident beam,
θ is the diffraction angle,
and β is the full width half maximum intensity of the diffraction peak.

From the XRD pattern, the calculated value of average crystallite size is 38 nm.

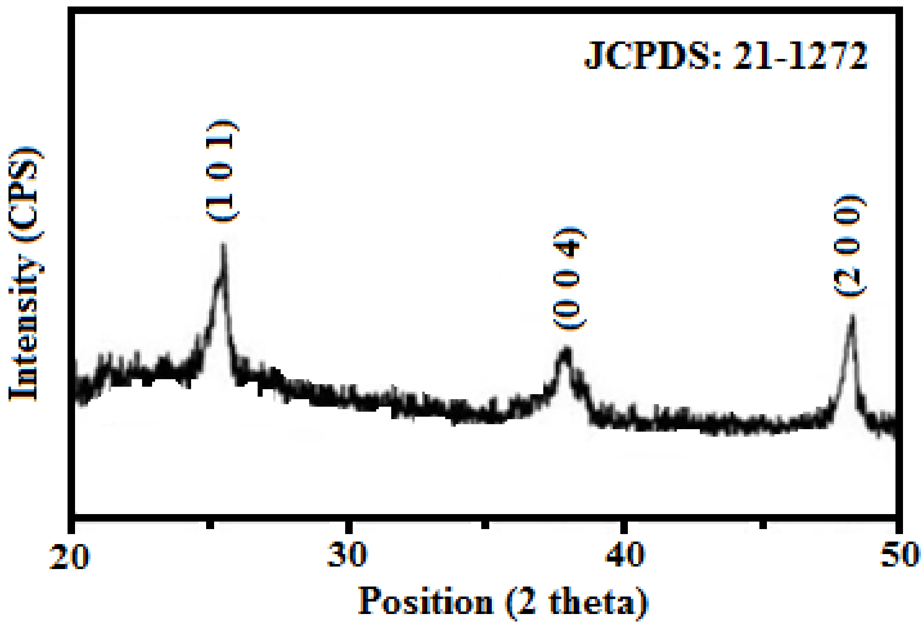

Figure-1: Powder XRD pattern of TiO_2 thin films

Morphological Studies

SEM and EDS analysis was used to study the morphology and chemical composition of as synthesized sample. Figure-2 shows the SEM micrographs of TiO_2 thin films taken at different magnifications. From low resolution SEM images, one can be clearly observe that the prepared sample shows agglomeration with an irregular morphology. The agglomeration could be induced by densification resulting from the narrow space between particles. SEM reveals that the sample consists of irregular shaped sphere like structures. EDS measurements confirm the incorporation of manganese ions into the host material. Figure-3 shows EDS pattern TiO_2 thin films. The pattern showed the elemental compositions of Ti, O and manganese. From this it was confirmed that the sample contains doped manganese species. The nanocrystalline nature of the samples was confirmed by TEM measurements. The TEM image of TiO_2 thin films was depicted in Figure-4. The particles are more or less uniformed in size with irregular shape.

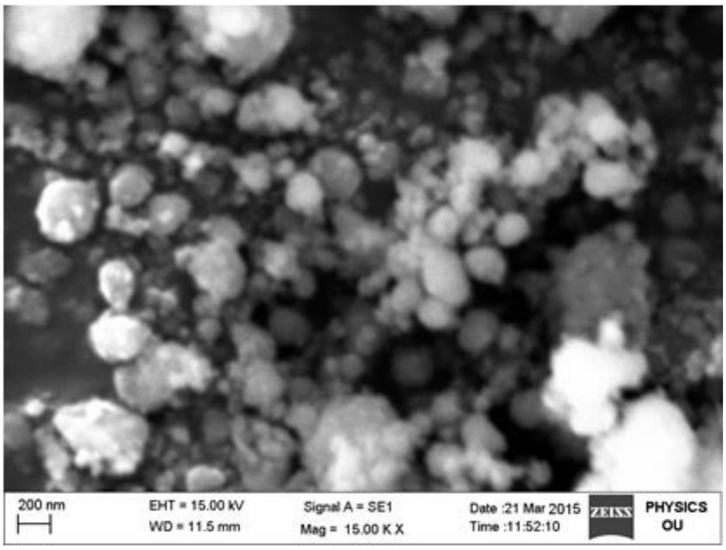

Figure-2: SEM image of TiO_2 thin films

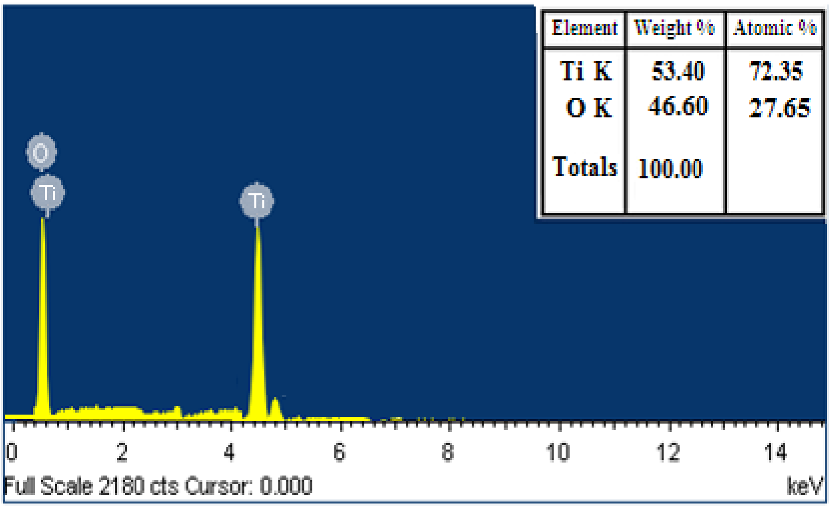

Figure-3: EDS spectrum of TiO_2 thin films

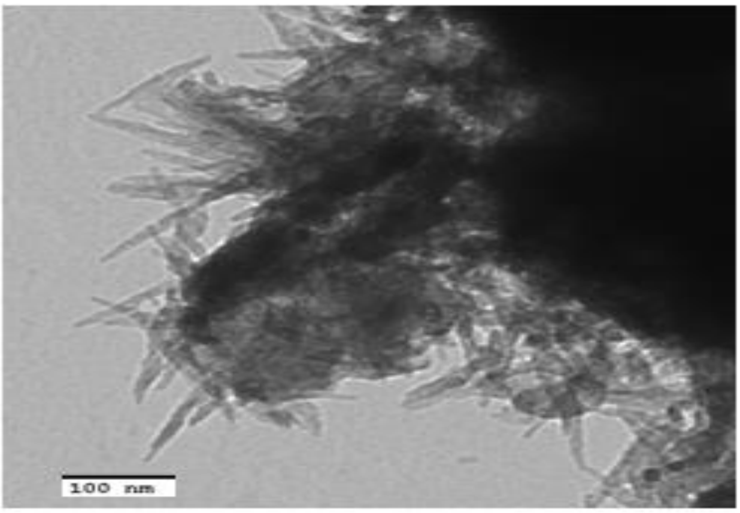

Figure-4: TEM image of TiO_2 thin films

FT-IR Studies

Figure-5 shows FT-IR characteristic peaks of surface functional groups of TiO_2 thin films. The spectrum shows absorption peak in the spectrum at 3450 cm^{-1} possibly attributed to the OH group (molecular water). Ti-O-Ti bands appear in the range 500-900 cm^{-1}. Additionally the bands at 2956, 2836 and 1425 cm^{-1} were assigned to C-H vibrations. The C-H bond could be of NH stretching vibrations [32].

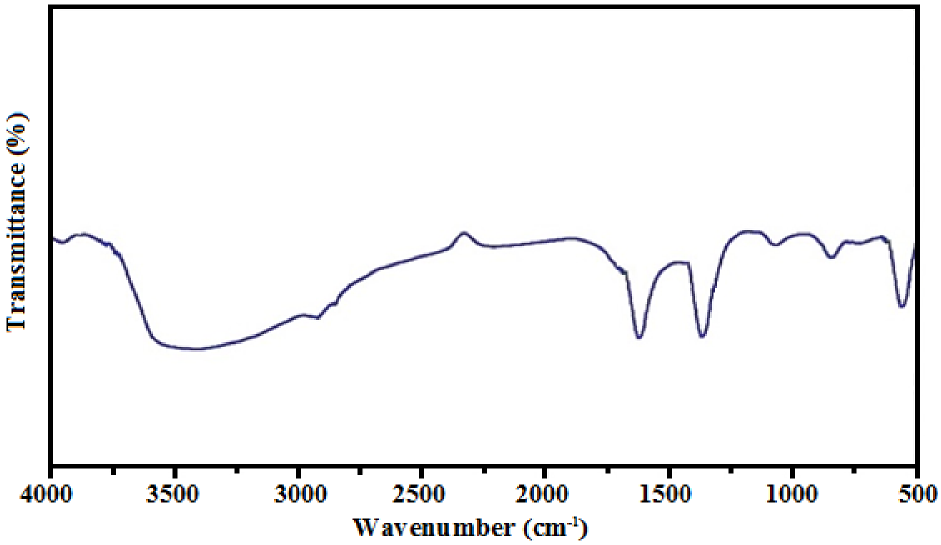

Figure-5: FT-IR spectrum of TiO_2 thin films

CONCLUSIONS

TiO_2 thin films were prepared successfully by sol-gel method. X-ray diffraction studies revealed the crystal system is indexed to be anatase crystalline state with JCPDS file No. 21-1272. The calculated average crystallite size of TiO_2 thin films is around 38 nm. SEM revealed irregular shaped sphere like structures and EDS confirms the presence of constituent elements in the host material. The formation of nanorods is confirmed by TEM analysis. The characteristic vibrational modes of host lattice are evidenced by FT-IR spectrum.

REFERENCES

[1] Kumar PM, Badrinarayanan S, Sastry M. Thin Solid Films 2000; 358: 122-130.
[2] Chee YH, Cooney RP, Howe RF. J Raman Spectrosc 1992; 123: 161-166.
[3] Guang-Lei T, Hong-Bo H, Jian-Da S. Chin Phys Lett 2005; 22: 1787-1789.
[4] Eiamchai P, Chindaudom P, Pokaipisit A. Curr Appl Phys 2009; 9: 707-712.
[5] Wang Z, Helmersson U, Kall PO.Thin Solid Films 2002; 405: 50-54.
[6] Jiang HQ, Wei Q, Cao QX.Ceram Int 2008; 34; 1039-1042.
[7] Du W, Wang H, Zhong W. J Sol–Gel Sci Technol2005; 34: 227-231.
[8] Ungureanu F, Medianu R, Ghita RV. J Optoelectron Adv Mater 2007; 9: 1457-1461.
[9] Van Bommel MJ, Bernards TNM.J Sol–Gel SciTechnol 1997; 8: 459-463.
[10] Nikolic LM,Radonjic L, Srdic VV. Ceram Int 2005; 31: 261-266.
[11] Li Z, Wu M, Liu T. Ultramicroscopy 2008; 108: 1334-1337.
[12] Hu L, Yoko T, Kozuka H.Thin Solid Films 1992; 219: 18-23.
[13] Lee HY, Kale GM. Int JAppl Ceram Technol 2008; 5: 657-665.
[14] Fujishima A, Honda K. Nature 1972; 238: 37-38.
[15] Kim T, Lee TK, Lee MN, Park SH. Thin Solid Films 2005; 475: 171-177.
[16] Angkaew S, Limsuwan P. Proce Engg 2012; 32: 649-655.
[17] Kiselev A. Surf Sci 2005; 584: 98-105.
[18] Taranto J. Sepa Purifica Tech 2009; 67: 187-192.
[19] Moon J. Sen Actua B: Chem 2010; 149: 301-305.
[20] Calabria J. Constru Build Mater 2010; 24: 384-389.

ISSN: 0975-8585

[21] Rao MC. Optoelect & Adv Mater (Rapid Commu) 2011; 5(5-6): 651-654.
[22] RaoMC, Ramachandra RaoK. Int J Chem Tech Res 2014; 6(7): 3931-3934.
[23] Rao MC. Int J Chem Tech Res 2014; 6(3): 1904-1906.
[24] Prasad PV, Ramachandra Rao K, Rao MC Int J Chem Tech Res 2014; 7(1): 269-274.
[25] Rao MC. Optoelect & Adv Mater (Rapid Commu) 2011; 5: 85-88.
[26] Muntaz Begum Sk, Rao MC, Ravikumar RVSSN. Spectrochim Acta Part A Mol & Biomol Spec 2012; 98: 100-104.
[27] Muntaz Begum Sk, Rao MC, Ravikumar RVSSN. J Inorg Organometa Poly Mater 2013;23(2): 350-356.
[28] Rao MC. J Optoelect & Adv Mater 2011; 13: 428-431.
[29] Rao MC, Hussain OM. Eur Phys J Appl Phys 2009; 48(2): 20503
[30] Ravindranadh K, Rao MC, Ravikumar RVSSN. J Luminesce 2015; 159: 119-127.
[31] Karabay I, AydınYuksel S, Ongül F, Ozturk S, Asli M. Acta Phys Polon A 2012; 121: 1- 14.
[32] Ravi RP, Krishan KS, Marshal D. J Biosens Bioelectron 2010; 1**:** 101-109.