Chemical Concepts

International Journal of Chemical Concepts
ISSN:2395-4256 www.chemconsai.com
Vol.03, No.02, pp 201-207, 2017

Investigation on TiO_2 thin films prepared by sol –gel spin coating method for photocatalytic application

T. Vasuki, M. Saroja, M. Venkatachalam, S. Shankar

Department of Electronics, Erode Arts and Science, College Erode-9, Tamil Nadu, India

Abstract : **T**iO_2 thin films were prepared on glass substrates by sol- gel spin coating method. Tiatanium tetra iso propoxide, ethanol and diethanolamine were used to prepare the coating solution. The prepared films were annealed at different temperatures of 350, 450 and 550°C. The structural properties were investigated by using X-ray diffraction technique and grain size was calculated. The optical properties were investigated using UV-Vis spectroscopy and PL studies and the optical band gap was calculated. The TiO_2 thin films prepared at 450°C were used as photo catalysts for photo catalytic degradation of methylene blue dye. A maximum efficiency of 88 % is reported.
Keywords: TiO_2 thin films, sol gel spin coating, UV-Vis absorbance, Photocatalysis.

1. Introduction

Titanium dioxide (TiO_2) has been widely used as a pigment[1] and in sunscreens,[2,3] paints[4], ointments, toothpaste,[5] etc. In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode under (UV) light.[6-8] Since then, enormous efforts have been devoted to the research of TiO_2 material, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-/ electrocromics and sensors,[9-15] These applications can be roughly devided into " energy" and "environmental " categories, many of which depend not only on the properties of the TiO_2 material itself but also on the modifications of the TiO_2 material host (e.g., with inorganic and organic dyes) and on the interactions of TiO_2 materials with the environment. Many applications of TiO_2 nanometerials are closely related to their optical properties. TiO_2 nanomaterials normaly are transparent in the visible light region. By doping or sensitization, it is possible to improve the optical sensitivity and activity of TiO_2 nanometerial in the visible light region.

2. Experimental

2.1 Preparation of precursor solution

TiO_2 thin films have been prepared onto well cleaned glass substrates by sol gel spin coating method. Titanium Tetra Isopropoxide (TTIP), Diethanolamine (DEA), and Ethanol (Merck) were used as starting material, stabilizer and solvent to prepare and were used without further purification. The relative volume ratio of each chemical in precursor solution was TTIP : DEA : C_2H_5OH = 3 : 1 : 20. The starting solution was prepared by mixing DEA with 10ml of ethanol followed by the addition of Titanium Tetra Isopropoxide (TTIP). After stirring this solution for 30min, additional 10ml of ethanol was added and the stirring was continued for 3hrs at room temperature to yield a clear and homogeneous solution. The resultant solution was stable for a period of seven days followed by the occurrence of gelation. All the chemicals used in the experiment were of analytical grade and were used without further purification.The pH value of this solution was observed as 7.5

2.2 Preparation of TiO_2 thin films

The prepared solution was dropped on the cleaned glass substrates and the substrates were rotated at 3000 rpm for 20s and the TiO_2 thin films were prepared by repeated coating. After each coating films were heated at 250°C for 5 min to evaporate the solvent and the organic residuals (named as pre-heat treatment). After the pre-heat treatment, the TiO_2 thin films were allowed to cool to room temperature to avoid crakes. The spin-coating and pre-heating process was repeated for seven times. The TiO_2 thin films were annealed in a furnace in air atmosphere at 350°C, 450°C and 550° C for 60 minutes and allowed to cool to room temperature gradually.

2.3 Characterization of thin films

The structural properties of the sol gel spin coated TiO_2 thin films have been studied using x-ray diffraction (XRD) analysis which was carried out using a XPERT-PRO with Cu Kα radiation at the Bragg angle ranging from 30° to 80°. From this analysis the grain size, and dislocation density have been calculated. Optical properties of prepared TiO_2 thin films were studied using a JASCO-570 UV –Visible Spectrophotometer. The photoluminescence properties of the TiO_2 thin films annealed at three different temperatures were characterized using Horiba Jobin Yvon Fluorolog-3 Spectrofluorometer System. Photocatalytic activity was carried out in a specially designed reactor in which the light source was 8W UV lamp (Philips TUV-08-G5) used.

The absorption spectra were recorded using JASCO V-570 UV-Vis Spectrophotometer and rate of decolorization was observed.

3. Results and Discussion

3.1 Structural Analysis

XRD Analysis of TiO_2 Thin Films Synthesized at Different Annealing Temperature

The structural properties of TiO_2 thin films were governed by deposition parameters and annealing temperature. In the present work TiO_2 thin films were prepared by sol gel spin coating method and they were annealed at different temperatures. The figure 1 shows the typical XRD pattern of TiO_2 thin films annealed at different temperatures of 350, 450 and 550°C. It is clear that no characteristic peak corresponding to impurities of the precursor was found.

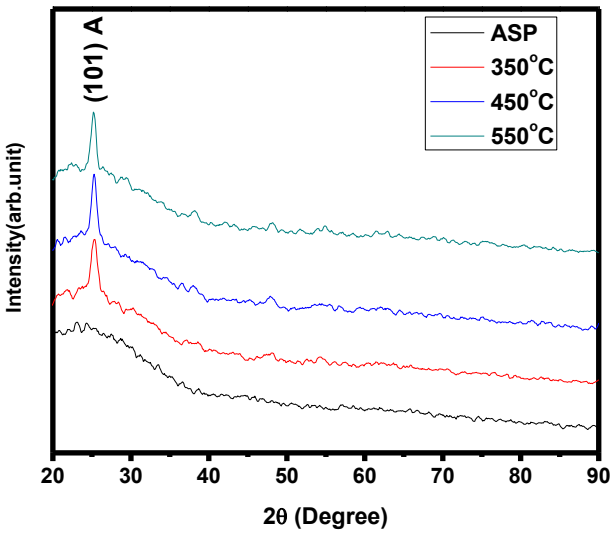


Fig 1 X- ray diffraction pattern of TiO_2 thin films annealed at three different temperatures.

Table 1 Structural properties of TiO_2 thin films prepared at three different temperatures. temperatures.

Annealing Temperature(^{0}C)	Grain size (nm)	Dislocation density × 10^{-3}(lines/m^2)
350	8.51	13.8
450	13.49	5.49
550	21.3	2.20

The XRD pattern of as prepared TiO_2 thin film is amorphous. As shown in the figure the peaks are appeared and the relative intensity of the peaks tends to increase and width of the peaks get decreased with increase in annealing temperature. The films annealed at450° C shows the maximum intensity. It seems that all annealed TiO_2 thin films possess a high crystallinity, since all peaks are very sharp. The increase in peak intensities indicates an improvement in the crystallinity of the prepared TiO_2 thin films. The peaks appear at 2θ values of 25.62^0, which correspond to the (101) plane. The data are in good agreement with the standard JCPDS card (89-4921) for TiO_2.

As the annealing temperature increases from 350°C to 550°C, the intensity of the (101) peak has been further increased. The diffraction pattern shows that the intensity of the (101) peak increase with increasing in annealing temperature. This is due to the improvement in the crystalline nature of the prepared TiO_2 thin films.

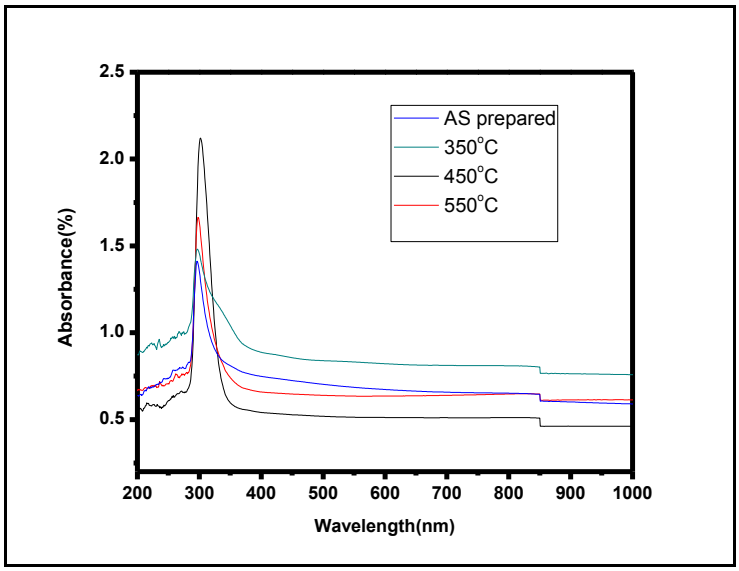


Fig 2 Absorbance spectrum of TiO_2 thin films annealed at different temperatures.

3.2 Optical properties

3.2.1 Absorption Spectrum Analysis of TiO_2 Thin Films Synthesized at different Annealing Temperatures

The optical absorbance properties of TiO_2 thin films were governed by deposition parameters and annealing temperature. In the present work TiO_2 thin films were prepared by sol gel spin coating method and they were annealed at different temperatures. Fig 2 shows the optical absorption spectra of TiO_2 thin films annealed at 350, 450, and 550°C. It can be seen that the intensity of the UV peaks increases with increase in the annealing temperatures and sharp peaks with maximum intensity in UV region are observed for the thin films annealed at 450°C, which might be due to the scattering of phonons by electron hole pairs. The absorbance edge is shifted to a higher wave length when annealing temperature is increased. It is well known that the optical absorbance determines the optical band gap and TiO_2 thin films have a direct band gap[16]. The optical band gap of TiO_2 thin films annealed at 350, 450, and 550°C was found to be 3.41eV, 3.25eV to 3.46eV respectively. The decrease in band gap of TiO_2 thin films may be attributed to the improvement in the crystalline quality of the films and increase in grain size. TiO_2 thin films prepared at 450°C shows smaller band gap and maximum UV absorbance intensity and hence the annealing temperature was optimized as 450°C for further studies.

3.2.2 Transmittance Spectrum Analysis of TiO_2 Thin Films Synthesized at Different Annealing Temperature

Transmittance spectra for the TiO_2 thin films annealed at different temperatures of 350, 450 and 550°C are shown in fig.3. As seen from the fig 3 as the annealing temperature increases, the transmittance of the films decreases. It has been shown that the absorption is due to transitions of electrons from top of the valance band to the bottom of the conduction band. Increase in density of site in the valance band with increase in annealing temperatures shifts the absorption edge to higher energies[17]. A decrease inaverage transmittance was observed with increase of annealing temperature and was attributed to the increase of surface roughness. The optical transmittance of TiO_2 thin films were found to decrease from 24% to 17% for the increasing temperature of 350, 450°C and 550°C.

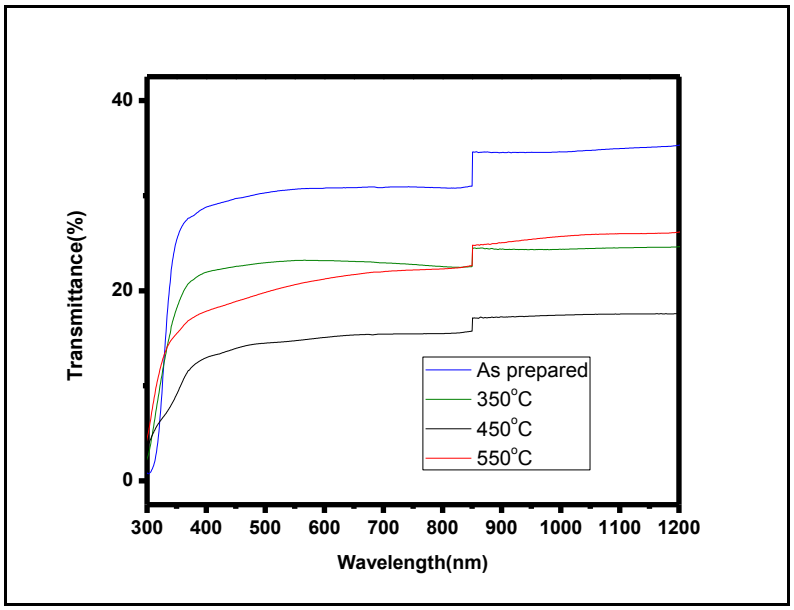


Fig 3.UV-Vis transmittance spectrum of TiO_2 thin films annealed at different temperatures.

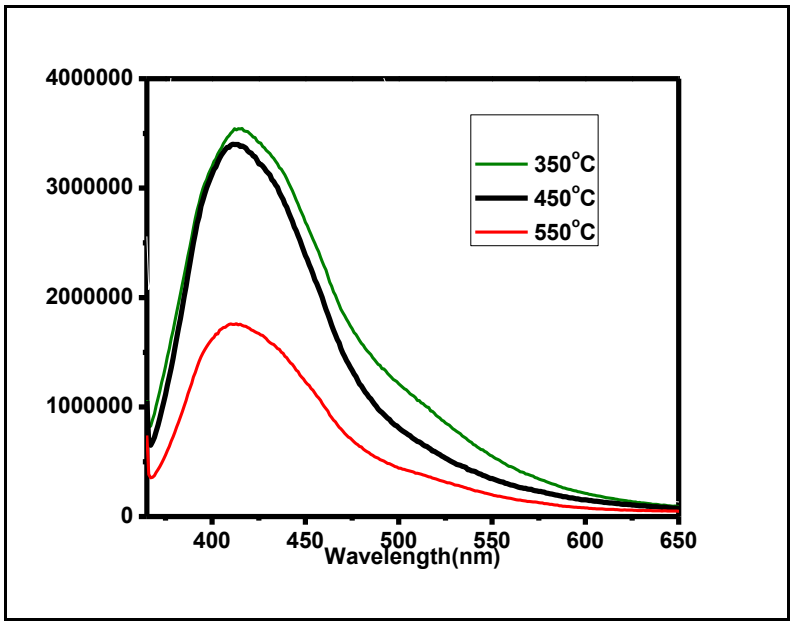


Fig4. Photoluminescence spectra ofTiO_2 thin films prepared at different annealing temperatures.

4. Photoluminescence Spectra of TiO_2 Thin Films prepared at different annealing temperature

The room-temperature PL spectra of the TiO_2 thin films annealed at different temperatures of 350, 450, and 550°C obtained with an excitation wavelength of 350 nm are shown in Fig 4. The ultraviolet (UV) emission peaks in the range of 396-400nm are present in all the PL spectra, the only difference being the relative intensity of peaks. It is observed that there is a shift in the position of peaks, which could be due to different native defects and free carrier concentrations in different samples.

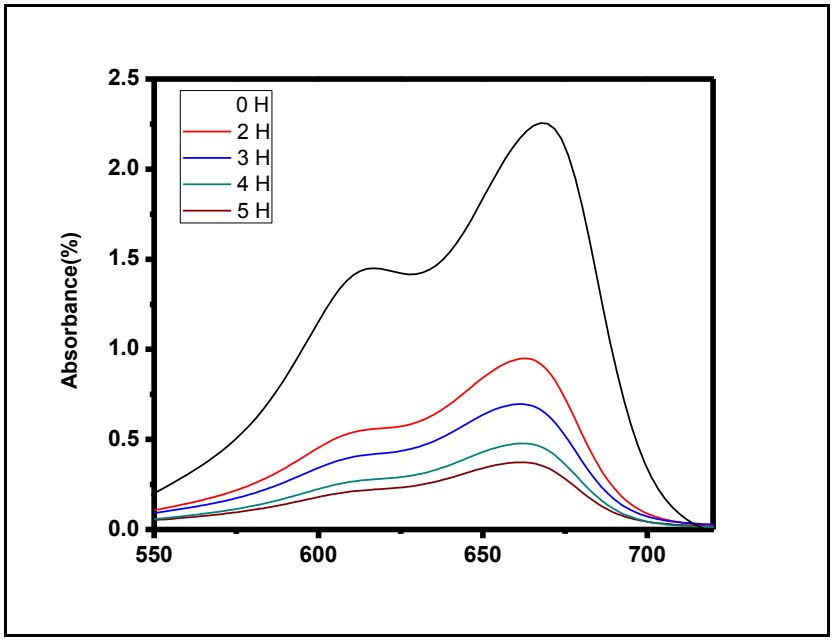
The UV peak is attributed to the recombination of free excitons through exciton - exciton collision process due to the 396nm (3.13 eV) wide band gap transition of TiO_2, and therefore indicates good crystallinity of TiO_2 samples . The samples annealed at 350,450 and 550^{0}C are showing visible emission centered at ~420nm (2.9eV).The strong emission (420 nm) resulted primarily from intrinsic defects. The intrinsic defects are associated with deep level emissions such as oxygen vacancies and interstitials. The oxygen vacancies and interstitials were induced by the thermal treatment process and sol-gel process.

5. TiO_2 Thin Films as Photocatalyst

Fig 5 shows the time dependent UV-Vis absorbance spectra of methylene blue dye during photo irradiation with TiO_2 thin film of 4 cm^2 area. The rate of decolourization was recorded with respect to the change in the intensity of absorption peak in visible region.

The prominent peak was absorbed at 665 nm which decrease gradually with increase in irradiation time from 2hour, 3hour, 4 hour and 5hour indicating that the dye had been degraded. The degradation efficiency of TiO_2 thin films prepared at 450°C was found to increase from 60%, 68.8% and 80% to 88% respectively for the irradiation time of 2hour, 3hour, 4hour and 5hour.

Fig 5.1 shows the effect of irradiation time on the de-colorization of methylene blue. It can be seen that the de-colorization of the dye gets gradually increased by increasing the irradiation time from 2hour, 3hour, 4hour and 5hour for methylene blue (MB).



Fg 5. Time – dependent UV-Vis absorption spectra for decolourization of methylene blue using undoped TiO_2 thin films

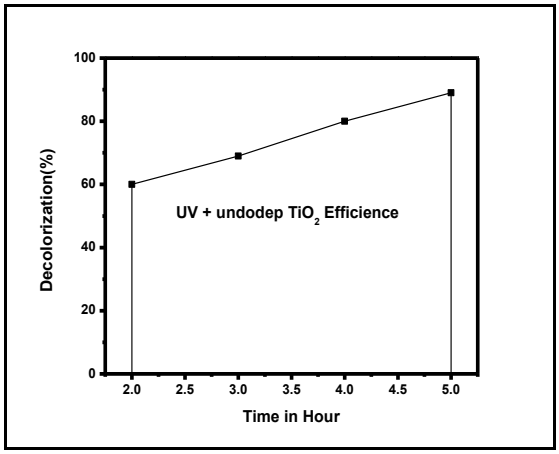


Fig 5 Photocatalytic de-colorization of methylene blue dye with various irradiation time using TiO_2 thin film annealed at 450°C.

Table 2. Photo degradation efficiencies of TiO_2 thin film annealed at 450°C with various irradiation time.

Irradiation time in hour	Degradation η (%) of undoped TiO_2
2	60
3	68.8
4	80
5	88

6. Conclusions

From the XRD investigations of undoped TiO_2 thin films it was observed that as the annealing temperature increases the grain size, crystanility get inceased and dislocation density gets decreased. TiO_2 thin films annealed at 550^0C shows maximum grain size, good crystallinity and minimal dislocation density. TiO_2 thin films annealed at 450°C shows higher intensity compared to 550°C.

From absorption spectra results of the TiO_2 thin films it is observed that the intensity of the UV peaks increases with increase in the annealing temperature from 350 to 550°C and sharp peak with maximum absorption intensity in UV region is observed for the film annealed at 450°C. The UV absorption results show that the band gap changes from 3.4eV, 3.25eVand 3.46eV with the increase of annealing temperature from 350,450 and 550°C. The decrease in band gap of TiO_2thin films may be attributed to the improvement in the crystalline quality of the films and increase in grain size.The UV transmittance studies show that the optical transmittance of TiO_2 thin films decreases as the annealing temperature increases. A decrease in average transmission was attributed to the increase of surface roughness. From the PL spectrum results, the undoped TiO_2 thin films prepared at 450°C have good number of oxygen vacancies and interstitial defects and it enhance the electron hole pair separation rate in TiO_2 thin films and are in favour of photocatalytic reactions. The photocatalytic activity was carried out on methylene blue by varying irradiation time of photocatalyst and respective degradation efficiencies were reported. Photocatalytic activity was carried out in a specially designed reactor in which the light source was 8W UV lamp (Philips TUV-08 G5). The maximum photo degradation efficiency for TiO_2 thin films were found to be 88 %.

Reference

1. Pfaff, G.; Reynders, P. Chem. Rev. 1999, 99, 1963.
2. Salvador, A.; Pascual-Marti, M, V,; Adell, J. R,; Requeni, A.; March, J. G. J.Pharm. Biomed. Anal, 2000, 22,301.
3. Zallen, R.; Moret, M. P. Solid State Commun. 2006, 137, 154.

4. Braun, J. H.; Baidins, A.; Marganski, R. E.Prog. Org. Coat. 1992, 20, 105.
5. Yuan, S. A.; Chen, W.H.;Hu, S. S.Mater, Sci, Eng, c 2005, 25, 479.
6. Fujishima, A.; Honda, K. Nature 1972, 37, 238.
7. Fujishima, A.; Rao, T. N.; Tryk, D.a.J. Photochem. Photobiol. C 2000, l, I.
8. Tryk, D. A.; Fujishima, A.; Honda, K. Electrochim. Acta 2000, 45, 2363.
9. Gratzel, M. Nature 2001, 414, 338.
10. Hagfeldt, A.; Gratzel, M. Chem. Rev. 1995, 95, 49.
11. Linsebigler, A. L.; Lu, G.; Yates, J. T.; Jr. Chem. Rev. 1995, 95, 735.
12. Millis, A.; Le Hunte, S. J. Photochem. Photobiol., A 1997, 108,1.
13. R.H. Bari, Selectivity of organic vapour for nanostructured CdO thin films prepared by sol-gel dip coating technique, International Journal of Chemical Concepts, 2015, 1 (3), 136-148.
14. R. H. Bari, S. B. Patil Improved NO_2 sensing performance of nanostructured Zn doped SnO_2 thin films, International Journal of Chemical Concepts, 2015, 1 (2), 86-96.
15. R. H. Bari S. B. Patil Ethanol sensing performance of nanostructured Zn doped $CdSnO_3$ thin films International Journal of Chemical Concepts, 2016, 2 (1), 01-11.
16. M. Haase, H. Weller, A.Henglein, J. Phys. Chem 92,482(1988).
17. P. R. Berman, Vol,45, Academic press, Amsterdam, (1997)

*****