International Journal of
Scientific Research in Science and Technology (IJSRST)
Print ISSN : 2395-6011, Online ISSN : 2395-602X
International Conference on Advanced Materials
Held on 14, 15 December 2017, Organized by Department of Physics,
St. Joseph's College, Trichy, Tamilnadu, India

Effect of Thickness on Catalytic Performance of Cu Doped TiO_2 Thin Films

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Abstract

Thickness plays a vital role in determining properties of thin films and its variation influences performance of the thin films remarkably. In this work, the impact of thickness on the structural, morphological and optical properties of Cu-TiO_2 thin films have been investigated in detail. Copper doped Titanium dioxide thin films with different thickness (~1.89 to 2.44μm) were deposited on glass substrates by sol gel dip coating technique and were annealed at 500°C for 3 h. The annealed films were subjected to different characterization studies. The surface morphology and stoichiometry of the prepared films were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) respectively. The microstructural parameters such as crystallite size, dislocation density and micro strain of deposited films demonstrate notable variations with increased film thickness. The optical absorption of Cu-TiO_2 thin films show shift towards long wavelength region depending upon thickness. The photocatalytic activity of the different layered thin films was also tested via the degradation of Methylene Blue (MB) and Methylene Orange (MO) dye solutions under visible irradiation. The threshold thickness for best catalytic efficiency was acquainted and reported.

Keywords: Cu-TiO_2 thin films, XRD, SEM, UV-Visible, Photocatalytic activity

1. Introduction

Due to the increase in the demand of thin films in diverse fields such as semiconductor device fabrication, optical coating, magnetic recording, photovoltaics and photocatalytic turn out thin film techniques as one of primary materials processing methods. The fundamental properties of thin films rely on deposition parameters such as film thickness, grain size and substrate quality. The transition metal oxide TiO_2 semiconductor possesses a range of applications in various fields due to its exceptional properties such as nontoxicity, high catalytic activity, low cost, and long-term stability [1, 2]. TiO_2 has been synthesized using numerous methods such as chemical vapor deposition (CVD), plasma, hydrothermal and sol-gel [3]. Among these methods, sol-gel is the simplest technique in which the different material parameters such as morphology, surface area, average crystallite size and phase structure can be controlled and extended in determining photocatalytic activity of TiO_2 compound [4]. Pristine TiO_2 has band gap energy of about 3.2eV. TiO_2 photocatalyst stimulates production of highly oxidative hydroxyl radicals (OH) and Super-oxide radicals (O_2-), resulting in the decomposition of any organic pollutants present in the environment through a natural occurring oxidation process. Thus, TiO_2 have gained considerable attention as a self-cleaning material for environmental purification and clean energy. The key factors governing the photocatalytic activity of TiO_2 are lowering of band gap energy in visible region and prevention of electron hole recombination rate. One of the methods to improve photocatalytic activity of TiO_2 in the long wave length region is doping metal impurities in the TiO_2 matrix or coupling low band gap semiconductor with TiO_2 [5-7]. The integration of metal ions in TiO_2 lattice bids a way to trap the charge carrier thus improving the efficiency of TiO_2 catalyst [8].

In this work, efforts have been taken to prepare Cu doped TiO_2 thin films of different thickness by sol-gel dip coating method and the influence of thickness on optical and catalytic properties of Cu-TiO_2 thin films was investigated effectively.

Materials and methods

2.1. Raw materials

Titanium (IV) isoproxide (TTIP, 99.95 %, Fluka Sigma-Aldrich), and copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) were used as raw materials to prepare Cu-TiO_2 thin films. Ethanol (C_2H_5OH, 99.9%, Merck Germany) was used as solvent in the preparation of samples.

2.2. Thin films preparation

Cu doped TiO_2 thin films of various thicknesses (5, 7 & 9 dipping cycles) were prepared via sol-gel dip coating method. In the beginning 2.8 ml of Titanium (IV) isoproxide (TTIP) was mixed with 20 ml of ethanol and the mixture was vigorously stirred at room temperature for 10 min. And then 0.6 ml of acetic acid was added drop by drop to this solution and the blend was stirred for another 10 min. A suitable amount of copper (II) nitrate trihydrate was added into this solution slowly. Eventually, it was stirred at room temperature for 90 min., until clear sol was formed. To fabricate 5 dip Cu-TiO_2 thin films, the sol was deposited on glass substrates by five dipping with the drawing speed of about 1.5 mm/s at room temperature and the process was repeated to obtain 7 & 9 dip thin film samples of different thickness. The coated specimens were calcined at the temperatures of 500°C for 3 h with a heating rate of 10°C/min. The thickness was measured by surface profile meter. The thickness of films of 5, 7 & 9 dip is about 1.89, 2.17 & 2.44 μm respectively.

2.3. Characterization

The crystallite size of the Cu-TiO_2 thin films prepared with different Cu concentrations were estimated by X–Ray Diffraction method (XRD) using X'PERT PRO X–ray diffractometer which was operated at 40 KV and 30 mA with CuKα1 radiation of wavelength 1.5407Å. UV–visible spectra were recorded in the range of 300 – 800 nm using the Schimadzu 1800 UV–VIS–NIR spectrophotometer. The surface morphology observation and elemental were done by Carl Zeiss and Supra 55 respectively.

The surface topology was studied using Atomic Force microscope (AFM) Nano surf Easy scan 2. The thickness of the film was measured using Mitutoyo Surfest SJ-301stylus profilometer. Photocatalytic activity of the prepared Cu-TiO_2 thin films was studied by examining the degradation of aqueous solution of methylene blue (MB) under visible light irradiation using 500-W halogen lamp.

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of Cu doped TiO_2 thin films are shown in Figure1. It confirmed the presence of anatase phase of tetragonal structure with high intensity peak in (101) orientation. The other orientations observed at (210), (200) and (105) for all samples with low intensities, agree with JCPDS file no. 89-4203. Cu compound phase cannot be found in the XRD peaks due to small amount of Cu doping. The calculated micro structural parameters such as crystallite size, micro strain and dislocation density are tabulated in Table 1. The variation in dislocation density and micro strain with the thickness of films is shown in Figure 2. The reduction in FWHM reveals that the crystallization becomes more perfect when the thickness of film was increased by depositing more layers of Cu-TiO_2 on the substrate [9]. It was also noted that dislocation density 'δ' and micro strain (μ) decrease with increasing number of coatings as stress is liberated by minimized stacking fault [10].

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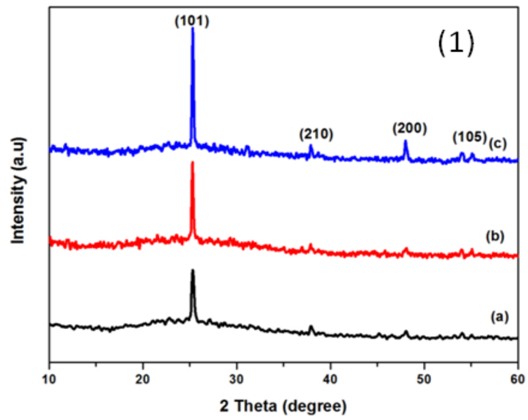

Figure 1. XRD patterns of Cu-TiO_2 thin films for different number of coatings

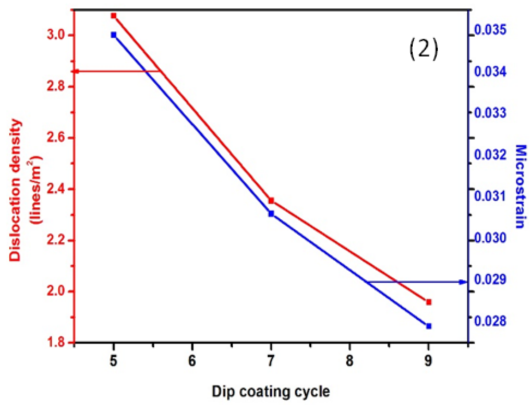

Figure 2. Variation of Dislocation density and Microstrain with different dipping cycles

Table 1. Micro structural parameters of Cu-TiO_2 films deposited at different dipping cycles

Dip coating cycles	Thickness (µm)	Crystallite size D (nm)	FWHM β	Dislocation Density δ x 10^{14} (lines/m^2)	Micro Strain ε	Bandgap (eV)
5	1.89	57.01	0.1432	3.0767	0.0349	3.14
7	2.17	65.15	0.1253	2.3558	0.0306	2.92
9	2.44	71.46	0.1094	1.9583	0.0279	2.79

3.2. Surface morphology and Quantitative Analysis

The surface morphology of deposited films was investigated by scanning electron microscope. Figure 3a & 3b show the SEM images of Cu doped TiO_2 thin films coated with 5 & 7 dip cycles. The images illustrate irregular flake like cracked morphology. During deposition, films undergo significant tensile stress which is relieved as cracks by annealing [11]. The surface cracks gradually rise with the increase in coating cycles. The EDAX picture shown in Figure 3c depicts only characteristic peaks of Ti, O and Cu elements.

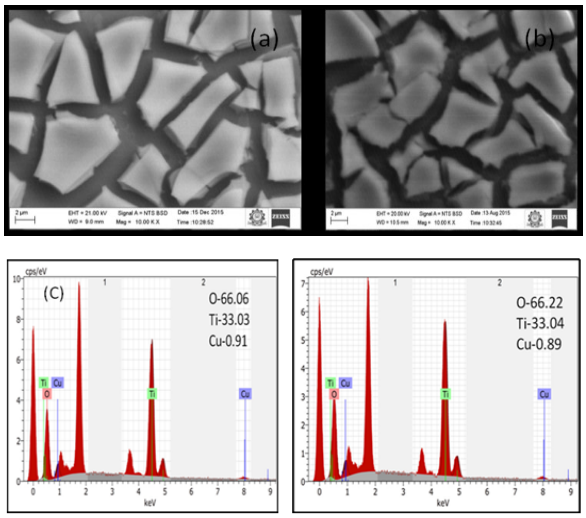

Figure 3. SEM images of the film deposited for 5 coatings (a) and 7 coatings (b) of Cu-TiO_2 thin films with EDAX spectrum (c)

3.3. Surface topography

Atomic force microscope was used to characterize the surface morphology and roughness of the deposited samples. The AFM image of Cu doped TiO_2 (9 dip) is shown in Figure 4. We can see dispersal of aggregated spherical grains of different sizes on the surface. The surface roughness parameters values such as the root mean square roughness (R_q) and average roughness (R_{ave}) are calculated as 11.26 nm and 8.567nm respectively.

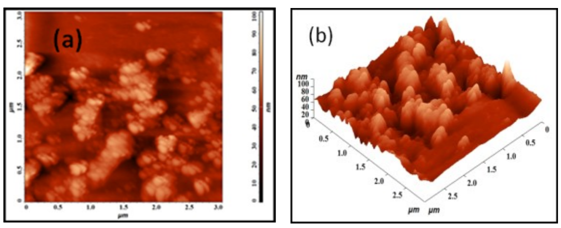

Figure 4. AFM (a) 2D and 5 (b) 3D image of Cu-TiO_2 thin films

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3.4. Optical analysis

The UV-Visible optical absorption spectra of the copper doped TiO_2 thin films are shown in Figure 5. Depositing more layers of Cu-TiO_2 films (5 to 9 dipping) resulted in shifting the absorption edge towards the visible region up to 440nm. The shift in the absorption edge is attributed to change in the crystallite size and thin film density with various thickness [12]. Also, the absorption edge movement towards longer wavelengths represents a decrease in the bandgap of about ~0.35eV [13]. Thus, the addition of Cu-TiO_2 layers on the substrate alter the optical responses of samples, causing a decrease in the bandgap energy and resulting in wide range absorbance of visible light, which can be used in photocatalytic application.

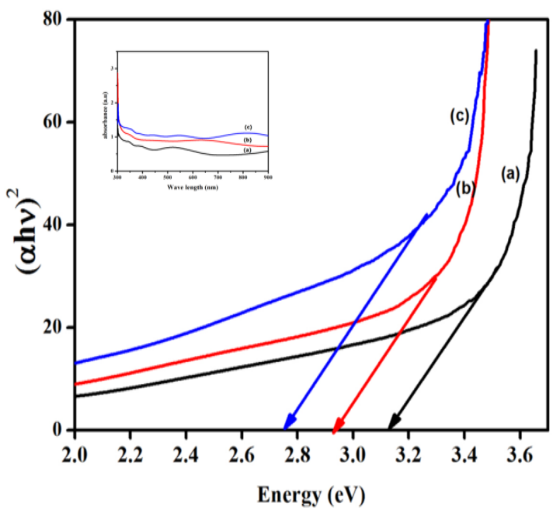

Figure 5. Direct bandgap of Cu-TiO_2 thin films (a) 5dip (b) 7dip & (c) 9dip

3.5. Photocatalytic activity

3.5.1. Thickness effect on photocatalysis

Photocatalytic activity of Cu doped TiO_2 thin films was analysed by examining the degradation of methylene blue (MB) and methylene orange (MO) dye solutions. The thin films were soaked into dye solutions and kept under visible light for irradiation. After that the 5ml of the degradation solution was taken and subjected to Schimadzu-1800 UV-Vis spectrometer to measure the absorbance.

To analyze the effect of thickness on catalytic performance, the thin films with different thicknesses were dipped into MB solution and kept under irradiation for 3hour.The absorbance spectra of degraded MB with Cu-TiO_2 thin films of different thickness are shown in Figure 6a. The reduced band gap energy and increased surface roughness (act as reaction sites) play important role in determining catalytic efficiency [14, 15]. It was observed that the photocatalytic activity of Cu-TiO_2 film was depending on the thickness. All the three films show degradation effect but the film with 5 coatings depicts the more enhanced catalytic activity than other films. The amount of photo generated electron hole pairs reaching the surface is abridged when thickness of the film increases above 1.89 µm. It was found that the thickness of Cu-TiO_2 (5-dip) film is optimum for better photo catalytic efficiency. The percentage of degradation of MB with the catalyst is shown in Figure 6b. The degradation effectiveness of samples decreases with the increase in thickness. The film with minimum thickness~1.89 µm shows the highest percentage of degradation about 80% than that of film prepared with the thickness of 2.44 µm.

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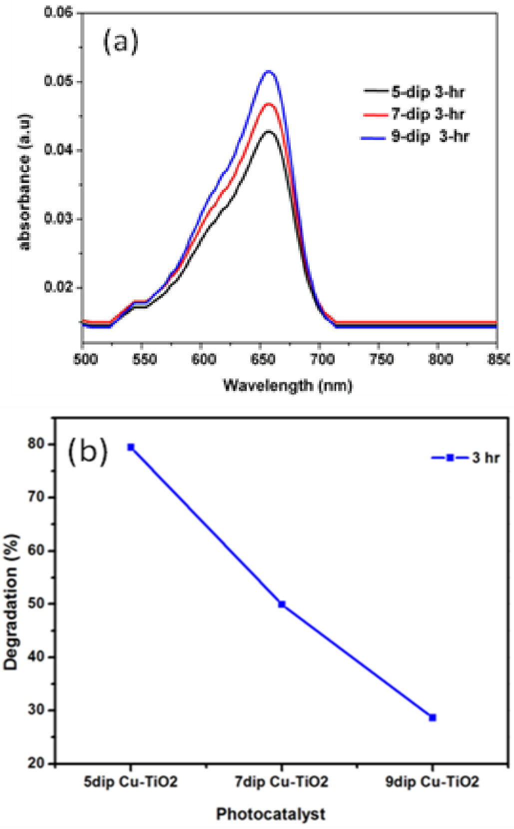

Figure 6 (a). Optical absorption spectra of degradation of MB dye thin films (b) Percentage of degradation of MB for different thickness of the films

3.5.2. Time Effect on photocatalysis

The degradation time effect on MB and MO dyes was examined by soaking Cu-TiO_2 thin films in MB and MO solutions respectively for 1, 2,3 and 4hour under visible light. The changes in the concentration of dye solutions MB and MO as a function of time with Cu-TiO_2 catalyst are shown in Figure 7(a & b). In photocatalytic activity, the degradation efficiency is more reliant on the illumination time. If the illumination time is longer, the degradation will be higher. The degradation efficiency increases with increase time with Cu-TiO_2 thin films. Figure 7c shows degradation percentage of MB & MO dye with the catalyst Cu-TiO_2 (5dip). It was seen that complete decomposition took place in MB solution after 240 minutes. Hence, the optimum illumination time for degradation of MB is 240 minutes. However, in MO solution, we could see still the presence of little dye after 240 minutes degradation. Thus, it is resolved is that Cu-TiO_2 catalyst was more efficient for the degradation of MB.

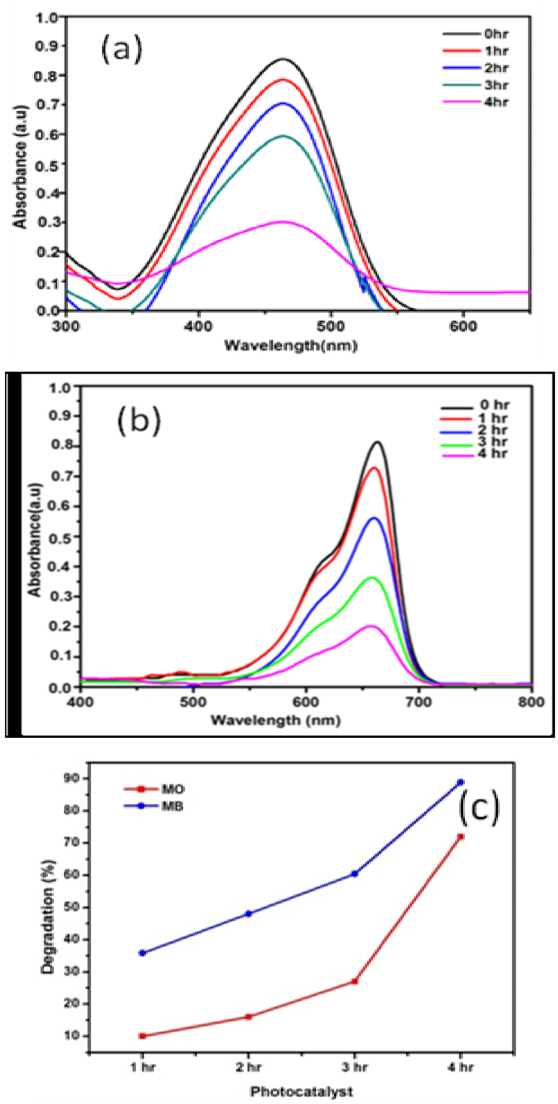

Figure 7 (a & b) . Optical absorption spectra of degradation of MO & MB dye thin films
(b) Percentage of degradation of MO & MB for Cu-TiO_2 films

4. Conclusion

This work reveals dependences of structural, optical and degradation properties on the thickness of Cu-TiO_2 films deposited onto glass substrates by dip coating technique. The thin films exhibited homogeneous surface grain aggregation, improvement in the optical activity and reduced bandgap energy. Degradation of MB dye solution under visible light rationalizes the dependence of thickness of Cu-TiO_2 thin films on the photocatalytic activity property. The film with ~1.8μm thickness (5-dip) show better degradation efficiency since only the excitons present in the surface region of few nm involves vigorously in photo catalytic reactions. Degradation time effect analysis shows that the film removes more MB molecules in short time. Hence it is proposed that Cu-TiO_2 thin film (~1.89μm) can act as an excellent photocatalyst under visible-light excitations.

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