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Synthesis and characterization of nanosized thin films of TiO_2 and ZnO and photodecomposition of hazardous dye by thin films

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ABSTRACT

Fabrication of high quality ZnO and TiO_2 thin films and analysis on its physical, chemical properties have application to remove dye from wastewater. In the present investigation highly textured semiconductor thin films were prepared by chemical bath deposition on glass substrate. The thin films were characterized by XRD, SEM analysis. The standard polycrystalline textured thin films contain nanograins were observed by XRD. SEM reveals the presence of adherent thin films. Photodecomposition of methylene blue from wastewater was possible by thin films.

KEYWORDS

Chemical deposition;
TiO_2 and ZnO thin films;
XRD;
SEM optical properties.

INTRODUCTION

Recently more attention has paid towards Zinc oxide and Titanium dioxide due to its vital property for various valid application. TiO_2 has been one of the most extremely studied oxide because of its role in various application, namely photo-induced water splitting, dye synthesized solar cells, environmental purification, gas sensors, display devices, batteries[1,6]. Fabricating high quality ZnO thin film substrate and the analysis on its physical and chemical properties will be important for the application such as energy efficient windows, liquid crystal display, opto-electronic devices, piezo-electric devices, acoustic electrical laser diode sensors[7-9]. Several techniques such as thermal oxidation[10], electron beam evaporation[11], activated reactive evaporation[12], spray pyrolysis[13], metal organic chemical vapour deposition (MOCVD)[14], electrodeless bath[15], pulse laser deposition[16], RF magnetron sputtering[17] and chemical deposition[18] have been used for forming ZnO thin films. A lot of solution methods are developed for the deposition of TiO_2 thin films and many new techniques are being developed[19,20]. The TiO_2 nanoparticles have been prepared by chemical method using hydrolysis of $TiCl_4$, $Ti(SO_4)_2$ and TiI_4[21-24]. Many workers[25] have prepared nanocrystalline thin films with anatase crystal structure of TiO_2 by the cathodic electrodeposition.

Among the various methods chemical deposition is advantageous on account of its suitability for forming large area thin films. Chemical deposition of ZnO and TiO_2 thin films from an aqueous solution is a versatile method due to its simplicity and economy. In this paper structural, optical and surface morphological properties of chemically deposited TiO_2 and ZnO thin films were investigated.

EXPERIMENTAL

The chemicals such as $TiCl_3$ solution and NH_3 were used for the solution preparation. $TiCl_3$ solution was taken into a beaker and its pH was adjusted in between 11 and 12 by 20% diluted NH_3 with constant stirring .TiO_2 film has been deposited on a substrate by slow hydrolysis of $TiCI_3$ solution[26]. The increasing in pH, the rate of hydrolysis increased, which resulted into TiO_2 precipitation formation in the bulk of solution without film formation on the substrate. In chemical bath deposition reaction takes place between dissolved precursors generally in aqueous solution at lower temperature. When the solution is saturated, the ionic product is equal to solubility product and when it exceeds ions combine on the substrate introduces a degree of heterogeneity that facilitates nucleation in film growth process. Deposition of TiO_2 was carried out on previously cleaned glass substrate. All the experiments were performed at room temperature. After 18 hrs the thin films were taken out of bath washed with triple distilled water and dried under air flow.

Sodium zincate bath was prepared by mixing requires volume ratio of $ZnSO_4$ and NaOH solution. Before deposition the glass substrate were cleaned chromic acid followed by double distilled water. The cleaned substrate was alternatively dipped for specific period in sodium zincate bath and water bath kept at room temperature and near boiling point respectively. The complex layer deposited on the substrate during the dipping in sodium zincate bath will be decomposed to ZnO which dipping in hot water.

$$Na_2ZnO_2 + H_2O \rightarrow ZnO + 2NaOH$$

Part of the ZnO so formed was deposited onto the substrate as strongly adherent film and remainder formed as precipitate[27]. After required number of dippings, the substrate with the deposited ZnO thin film was annealed in air at 250°C for 30 min. The deposition kinetics of TiO_2 and ZnO thin film was analyzed by employing X-ray diffractometer, energy dispersive by x-ray, scanning electron microscope and UV-visible spectrophotometer.

The photocatalytic activity studies of the ZnO and TiO_2 thin films were carried out at room temperature. The film catalyst was immersed in a quartz cell containing 3.5 ml of an aqueous solution at 20 ppm of methylene blue. The methylene blue solution was irradiated in a photocatalytic reactor with mercury lamp (PHILIPS-400 watt) with an intensity 37.4 mW/cm^2. The reaction rate was followed by taking samples every 15 min. and analyzing them by UV-Visible double beam spectrophotometer (Systronics model-2203). The concentration of methylene blue was calculated from the absorption band at 665 nm by means of methylene blue.

TABLE 1 : Values of the apparent velocity constant stirring

Film	k (min^{-1})
TiO_2	3.87E-4
ZnO	2.26E-4

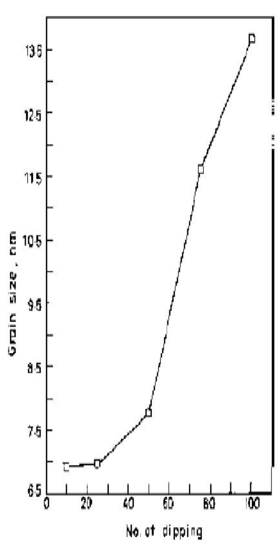
RESULTS AND DISCUSSION

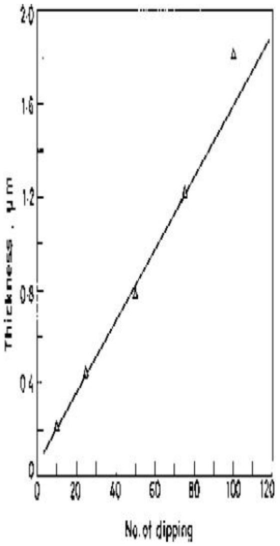
The deposition is feasible only when the molar concentration of the bath is less than 0.25 M. Due to the white precipitate of $Zn(OH)_2$ having large size clusters leaving a clear and water like solution on the top made the deposition unreliable and non-uniform even under stirred condition in baths having molar concentration greater than 0.25 M. Decreasing the concentration of the bath led to size reduction in $Zn(OH)_2$ clusters and enhances its distribution in the solution more uniformly. Deposition experiments conducted under this condition resulted ZnO thin film having uniform distribution throughout the substrate and bearing adherent nature. The physical verification on the deposited film indicated the near optimised experimental parameters when the molar cocentration is 0.167 M.

Figure 1 shows the X ray diffraction pattern of TiO_2 films. All diffraction pattern exhibit peaks of great width in the regions corresponding to the main peaks of TiO_2 region. This behavior indicates that the partial composite has been formed. This is probably due to short period and low temperature of the thermal treatment which are not optimal to produce a good crystalline state of the films.

The SEM images of the TiO_2 and ZnO thin films are shown in figure 2 as can be observed the morphology of the TiO_2 and ZnO films are homogenous.

The absorption of spectra (Figure 3) clearly exhibits the changes in the absorbance edges corresponding to the energy band gap TiO_2 (3.54 eV) and ZnO





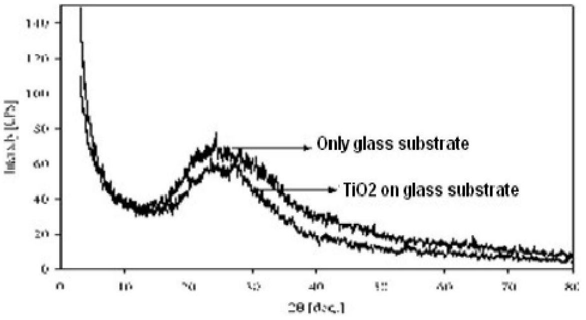
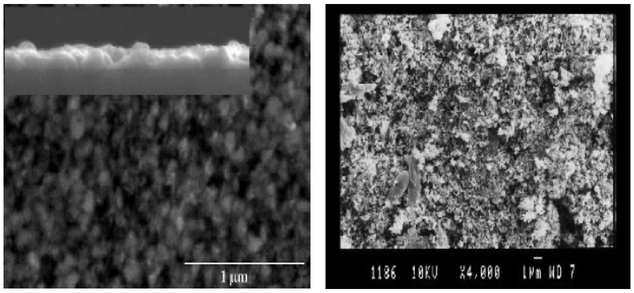


Figure 1 : XRD patterns of only glass substrate and TiO_2 on glass substrate



(A) (B)

Figure 2 : (A) SEM image of TiO_2 and (B) SEM image of ZnO

(3.17eV).

By keeping the concentration of bath as constant at 0.167M ZnO films were prepared for 10, 20, 50 and 100 number of dipping. The determined thickness of the deposited ZnO film over no. of dippings was present in the figure 4. The evolution of the methylene blue concentration as function of the photoreaction time with TiO_2 and ZnO catalyst is presented in

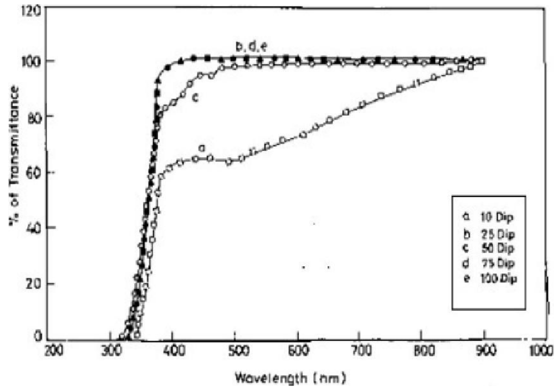


Figure 3 : Optical transmission of ZnO thin films for different number of dippings

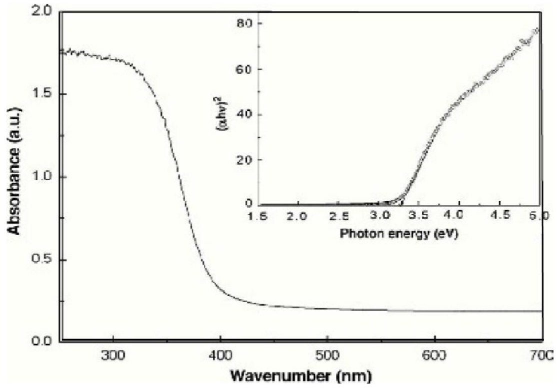


Figure 4 : Optical transmission of TiO_2 thin films for different number of dippings

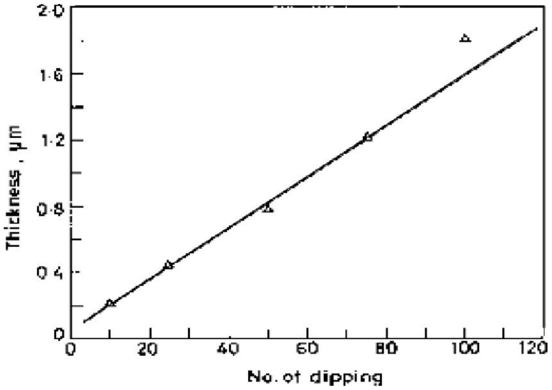


Figure 5 : A plot between film thickness and number of dippings

figure 4. The photocatalytic activity of thse films sohws an exponential decrement of the methylene with respect to time thus for correct data processing the Langmuir-Hinshelwood model for a reaction of first order and for heterogeneous photocatalytic reactions was applied.

$R = - dC/dt = k'C$

By integrating this equation we obtain,

$-\ln C/C_o = k't$

where r is the reactive disappearance velocity, C is the concentration at time t. C_o is the initial concentration and k is the velocity constant. The graph of $-\ln(C/C_o)$ vs time with the different catalyst shown in figure 5.

CONCLUSION

This communication demonstrates that nanocrystalline TiO_2 and ZnO thin films have been synthesized successfully using chemical de[position method at room temperature. The films are mechanically stable. The choice of the non heat resistance substrate such as glass substrate which should be beneficial for for photocatalytic applications. The XRD and SEM results indicates the composites film are amorphous. The TiO_2 and ZnO thin films present photocatlytic activity in the decomposition of methylene blue. The photodecomposition grade still low and is probably due to thickness of the films.

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