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Influence of Calcination Temperature for Optical and Photo Catalytic Properties of TiO_2 Thin Films Prepared by EB-Gun and Sol-Gel Method

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Abstract

In this paper we are presenting the remarkable TiO_2 nano photocatalytic material. The TiO_2 nano thin flms were deposited on glass substrate using PV-EBE method as well as sol-gel spin coating technique. The existed specimen shows nano-sized crystalline anatase phase. The optical and photocatalytic properties of the EBE and SGD films were compared. The reflectance of the films increased with increasing calcinations temperature from 3000°C and 5000°C as a result of the growth of particles. The refractive index of the SGD films increased significantly from 1.78 to 2.118 after heating at 5000°C were as that of EBE films increased slightly from 1.9 to 2.1. SGD films exhibited better photo activity then EBE films this has been explained in terms of porosity and the formation of Ti^{3+} ions during calcination, where EBE films had better optical activity then SGD films.

Keywords: Electron-beam Evaporation (EBE); Sol-Gel Deposition (SGD), Thin films, Photo activity

Introduction

Titanium dioxide (TiO_2) has drawn much attention recently in the field of photocatalysis. Titania is a wide band gap semiconductor with many interesting properties, such as transparency to visible light, high refractive index, and low absorption coefficient. Other than these properties, its eminent capability of photocatalytic decomposition of organic materials has come to utilization in the environmental business, i.e., organic pollutant treatment. To extend its applicability, the ease of production and reproducibility has to be secured in terms of production cost and product quality. TiO_2 films have been prepared by various vacuum techniques such as physical vapor deposition [1,2], and precipitation [3,4].

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The alkoxide sol-gel process [5] has emerged as one of the most promising techniques for growing TiO_2 thin films. The properties of TiO_2 films depend strongly on their microstructure that should be strictly controlled in order to obtain a tailored performance. The sol-gel coating method is one of the promising methods because the microstructure of the film is easily controlled by changing the solution composition and deposition condition. In addition, it provides uniform porous TiO_2 films with the large specific surface area, which is favorable in achieving good photo activity. In the present study, TiO_2 films on soadlime glass were prepared by EBE and sol-gel spin-coating methods. The optical and photocatalytic properties of the EBE and SGD films were investigated. The deposited TiO_2 films were characterized using UV-visible-ray diffraction and (XRD).

Experimental Techniques

TiO_2 thin films were deposited on soda lime glass by EBE and SGD methods. Prior to coating, the glass substrate was rinsed with acetone and then washed thoroughly with deionized water. EBE TiO_2 films were deposited in a vacuum chamber equipped with an electron beam gun. A detailed description of the experimental configuration is given elsewhere [6-13]. Titanium dioxide films were deposited in a conventional high vacuum deposition unit evacuated by a diffusion pump and rotary pump combination. The base pressure of 5×10^{-6} torrs is routinely obtained in two hours. The starting materials TiO_2 pellates (~Balzers, 99.8%) were vaporated using an electron beam gun ~ESV-6, Leybold Hereaus. The desired oxygen pressure was maintained by using a needle valve and measured with a hot cathode ionization gauge the substrates used were soda lime glass plates of 25 mm diameter and 2 mm thick. These were mounted on a spherical work holder and rotated to get uniform film thickness. The substrates were heated to 1800°C .Film thickness and the rate of deposition were monitored using a quartz crystal monitor (FTM 3, Edwards), whereas an optical monitor (OMS 2000, Leybold Hereaus) was used to monitor the in situ film transmittance of the films. The spectral transmittance of the films in the air was recorded using a UV-Visible Spectroscopy Shimadzu, UV-1650 PL model Preparation of the SGD sol is described elsewhere in detail [14].

The prepared sol was deposited on a sadalime glass substrate with spinning speed 3000 rpm at 60 seconds as deposited films were pre heated at half an hour at 800°C h and then calcinated at different temperatures from 3000°C to 5000°C for 3 hours in muffle furnance for modifying the porous morphology. The thickness of the films was measured by Envelope technique [15-17]. X-ray diffraction analysis of the films was carried out by X-ray diffractometer using Cu Ka radiation. The optical transmission and reflection spectra were recorded using UV-Visible Spectroscopy Shimadzu, UV-1650 PL model.

Results and Discussion

The reflectance of the TiO_2 thin film

In this study, the SGD films underwent the same heat treatment as the EBE films. The UV-Visible spectra of TIO_2 thin films prepared by EBE and SGD methods in the wavelength range 300-1000 nm bands of interference oscillation decreased with increasing calcinations temperature.

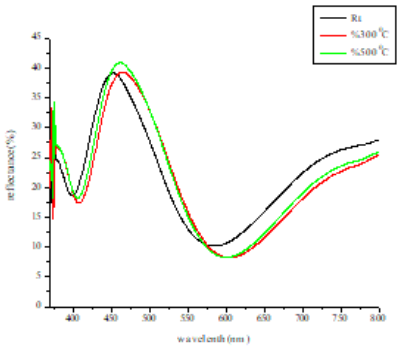

FIG.1. **The reflectance of EBE TiO_2 thin films a) RT b) 3000°C c) 5000°C**

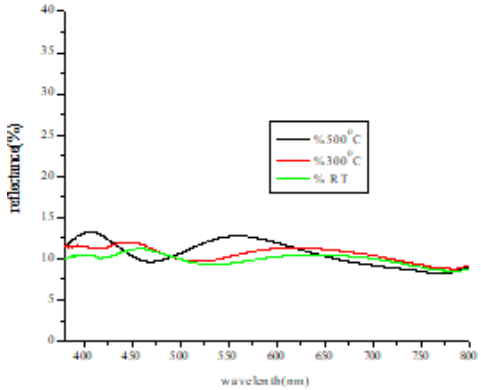

FIG. 2. **The reflectance of SGD TiO_2 thin films a) RT b) 3000°C c) 5000°C**

Also, the reflectance of TIO_2 thin films increased with increased as the calcinations temperature is raised from 3000°C to 5000°C.note that the reflectance of EBE films doesn't change at 3000°C and that of reflectance of SGD films increases at 3000°C .A significant increase in reflectance at 5000°C is attributable to the growth of particles. From the above **FIG. 1**. illustrates The refractive index and porosity of TiO_2 films are listed in **TABLE 1**. The refractive index of the prepared TiO_2 thin films was calculated from the measured reflectance spectrum. The evaluation method used in this work is based on the analysis of the reflectance spectrum of a weakly absorbing the film deposited on a non-absorbing substrate [12] refractive index n(k)over the spectral range is calculated by using:

$$n=\sqrt{ns}\{\sqrt{(1+\sqrt{Rp})/\cdot\sqrt{(1-\sqrt{Rp})}\}$$

The deposited EBE films of a thickness of about 540 nm and SGD films thickness about 380 nm estimated by envelope technique, It provides the best fits to the measured spectra. Deposited films are assumed to be homogeneous in the calculation. The porosity of the TiO_2 films is calculated using the following equation [13]

$$\{1-(n2-1/nd2-1)*100(\%)\}$$

Where nd is the refractive index of pore-free anatase (=2.52) [14] and n is the refractive index of the porous thin films. It is seen in **TABLE 1** that the refractive index of the SGD films increased from 1.789 to 2.1182 upon heating at 3000°C and 5000°C. The porosity of the SGD films decreased considerably from 58.83% to 34.83%. Accordingly, the SGD films are more porous than the EBE films by 15% at 3000°C. The small pores inside the SGD films have high sintering rates and the TiO_2 particles grow by intra-agglomerate densification leading to a significant drop in porosity at 5000°C [15]. The porosity of the dense EBE films is found to be relatively insensitive to the calcination temperature. **FIG. 2**. illustrates the XRD patterns of TiO_2 films calcined at different temperatures for 3 h. The XRD data indicate that SGD films are amorphous nature. The TiO_2 films calcined at 5000°C were identified as crystalline anatase.

TABLE 1. **The refractive index and porosity of TiO_2 films**

Temperature (°C)	**Refractive index SGD**	**Refractive index EBE**	**Porosity (%) SGD**	**Porosity (%) EBE**
Before calcination	1.9196	1.7895	58.54	49.83
300^0C	2.045	1.8381	58.41	40.52
500^0 C	2.124	2.1182	54.39	34.37

An MB aqueous solution of 8.12 lM was photocatalyzed in a quartz cell (10 × 10 × 9 × 45 mm^3) at 250°C. The TiO_2 film immersed in the solution was irradiated by the 365-nm UV lamp (130 lW/cm^2). A Shimadzu UV-1700 UV-Vis spectrophotometer was used to measure absorption spectra of the MB aqueous solution as a function of the 365-nm UV irradiation time. Film-type photocatalysts generally have lower surface areas than powered ones and thus the intrinsic photo activity of films is usually smaller than that of powders [16]. Secondly, in the case of SGD films, Ti^{3+} ions are formed during calcination and it was confirmed by the XPS data as shown in **FIG. 3**. From the above result of the reduction of Ti^{4+} to Ti^{3+} whioch helps the degradation of organic residues such as alcohol and unhydrolyzed alkoxide group. Organic residuals draw oxygen atoms from surrounding TiO_2 network. Ti^{3+} ions on the surface of the TiO_2 films may trap the photogenerated electrons, which are transferred from Ti^{3+} surface states to O_2 adsorbed on active sites of Ti^{3+}. This results in the reduction of recombination of photogenerated electrons and holes. The formation of a larger amount of Ti^{3+} ions contributes largely to the enhancement of the photoactivity of the TiO_2 films [16,17]. On the other hand, Ti^{3+} ions may not form in the case of the EBE films. Jiang et al. [18]. However, the long heating in air results in a decrease in the specific surface area, which also limits the photocatalytic activity of TiO_2 films [19]. XRD patterns of TiO_2 films deposited on glass substrates show peaks of anatase at 5000°C, whereas the annealing temperature of more than 5000°C was not attainable for photocatalyst **(FIG. 4-6).**

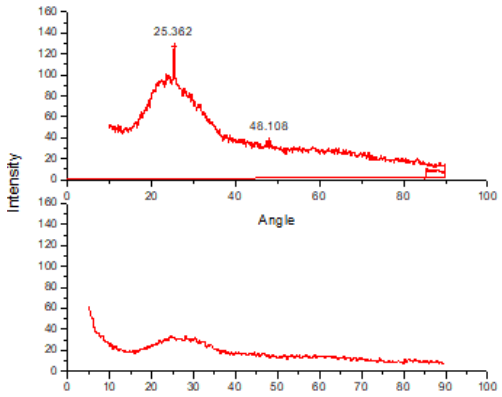

FIG. 3. **XRD spectra of EBE TiO_2 thin film calcined at 3000°C and 5000°C**

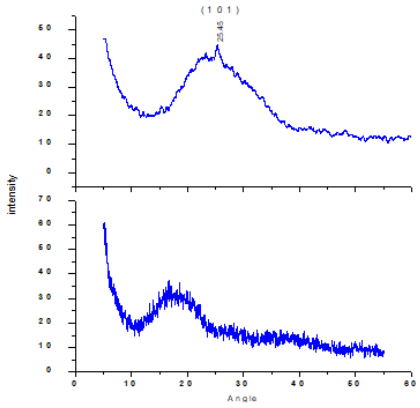

FIG. 4. **XRD spectra of SGD TiO_2 thin film calcined at 3000°C and 50000°C**

As seen before, XRD patterns of TiO_2 films deposited on glass substrates show no peaks of anatase up to 3000°C. The annealing temperature of more than 5000°C was not attainable. Therefore, the TiO_2 films of rutile crystal were not used as a photocatalyst in the present study. The results indicated that the heat treatment temperature and its duration can influence the rate of photodegradation. The samples were all in the complete anatase phase at 5000°C and showed the best rate of degradation. It has been found reportedly The photocatalytic activity of TiO_2 varies with its structural form and is higher in the anatase form compared to the rutile form [20,21].

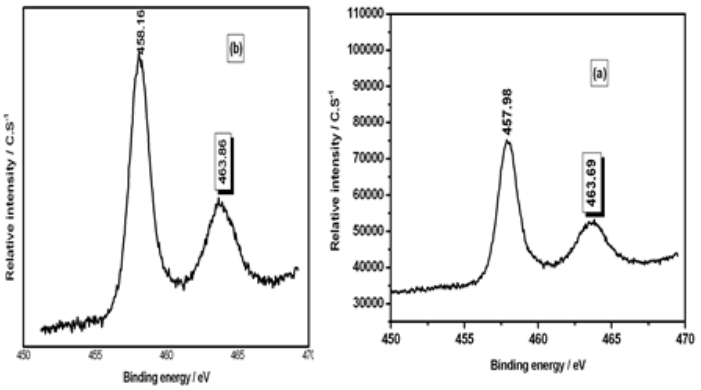

FIG. 5. **XPS Spectra of Ti^{+4} and Ti^{+3} ions in SGD TiO_2 thin film**

PhotoCatalytc degradation

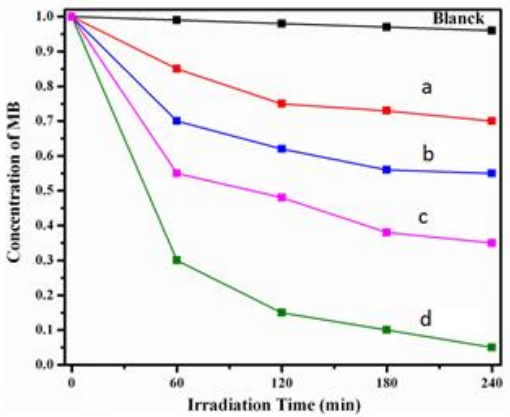

FIG. 6. **Photocatalytic degradation of methylene blue a) 3000°C EBE TiO_2 thin Film, b) 5000°C, C) 3000°C SGD TiO_2 thin d) 5000°C SGD TiO_2 thin film**

Conclusion

Optical studies revealed that the refractive index of the as-deposited SGD films increased considerably upon heating at 500°C shows effective Photodegradation of methylene blue , carried out under UVA irradiation, indicated that the degradation was effective only in the presence of the TiO_2 photocatalyst. Further, the photodegradation was found to be strongly dependent on the crystalline nature and crystallite sizes of the films. The SGD TiO_2 films were found to be superior in photo activity because of the formation of Ti^{3+} ions and high porous films than EBE TiO_2 films.

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