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# Photocatalytic and optical properties of titanium dioxide thin films prepared by metalorganic chemical vapor deposition

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ABSTRACT

Titanium dioxide thin films have been deposited by metalorganic chemical vapor deposition (MOCVD) over sodalime glass substrates at substrate temperatures ranging from 250 °C to 450 °C. The effect of deposition temperature on the structure and microstructure of the obtained films has been studied by x-rays diffraction (XRD) and scanning electron microscopy (SEM), respectively. Diffraction patterns show the existence of a pure anatase phase beside a texture change with the increase of deposition temperature. Micrographs show grain fragmentation with the increase in deposition temperature. UV–Vis. spectra have been recorded by spectrophotometery. The optical energy gap has been calculated for the deposited films from the spectrophotometrical data. Photocatalytic experiments have been carried out. The photocatalytic activity has been found to decrease with the increase in deposition temperature.

## 1. Introduction

Titanium dioxide is a preferable metal oxide for photocatalytic applications because of its non-toxicity and low cost. It can be prepared in the thin film form by many techniques, for example sol-gel [1,2], spray pyrolysis [3], sputtering [2], pulsed laser deposition [4] and chemical vapor deposition [5,6]. Thin film form is more suitable for photocatalysis because it enables the reuse of the photocatalyst without the need to separate it from the medium in which it was working [7]. In addition, oil slicks or spills can be treated easily by using thin films [8,9]. Titanium dioxide has three polymorphs; anatase, rutile and brookite. Rutile is the stable phase at high temperatures which can be obtained either by annealing [10] or increasing the deposition temperature [11]. Anatase forms at lower temperatures and its stability has been attributed to surface energy considerations [11]. It shows a superior photocatalytic activity when it has been compared to rutile [12,13].

The basic idea behind catalytic reactions in semiconductors like $TiO_2$ is that the absorption of light induces the transition of electrons from valence band to conduction band provided that the absorbed photon energy is equal to or greater than the optical energy gap. The produced electrons leave an equal number of holes in valence band. There are two explanations for the oxidation and reduction of the adsorbed species. First, electrons (or holes) reduce (or oxidize) adsorbed organic or inorganic acceptor (or donor) species existing on the surface of the semiconductor directly. Secondly, indirectly, when photogenerated electron–hole pairs react with water in aqueous media giving hydroxyl radicals, superoxide radical anions and hydroperoxyl radicals, which oxidize the organic pollutants on the surface of $TiO_2$ [14].

Many factors affect the catalytic performance of $TiO_2$. Surface and bulk recombination participate in controlling the catalytic activity. Recombination decreases the photocatalytic activity. The surface to the volume ratio plays a significant role in the performance of photocatalytic nanoparticles. The increase of this ratio raises the photocatalytic performance. Another factor that affects the catalytic performance is the optical band gap. The increase of the optical band gap enhances the redox potential of valence band holes and conduction band electrons. But, as the band gap increases the ability of the photocatalyst to absorb higher wavelengths decreases. Surfaces are defective sites so, recombination increases with the increase of surface area. Better crystallinity reduces the bulk defects which in turn improve the photocatalytic performance. Higher crystallinity can be obtained by annealing, which changes the surface area. Consequently, the determination of one factor playing the essential role in photocatalysis is impossible; instead we can talk about optimum conditions which can vary from one case to another. In this study pure anatase has been obtained and the crystallite size and crystallinity have been controlled by varying the deposition temperature. Effect of the deposition parameters on the photoctalytic performance of the obtained films has been discussed.

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## 2. Material and methods

Details about the MOCVD system used in this study have been described elsewhere [15]. Preparation conditions have been reported in a previous publication [6]. In summary, a horizontal hot wall MOCVD system consisting of a stain steel tube, a furnace, a mechanical pump, a pressure gauge, a gas flow meter, and a heating mantle for evaporating the precursor has been used. Argon gas has been used to carry the precursor (titanium tetra isopropoxide) to the reaction chamber while oxygen gas has been introduced to increase the rate of reaction. Sodalime glass substrates have been used for deposition at temperatures ranging from 250 °C to 450 °C at a total pressure of 15 Torr.

Morphology and thickness of the films have been measured by scanning electron microscopy using a JEOL JSM 7400F (FESEM). Optical transmission measurements have been carried out in a Perkin Elemer LAMDA 35 UV–VIS spectrophotometer over the range of 300–800 nm.

500 cc of an aqueous solution containing 100 ppm of high purity 2-chloerophenol has been subjected to UV irradiation using 6 W lamp at a wavelength of 254 nm. All photodegradation experiments have been conducted in a batch reactor at pH 6. The UV lamp has been placed in a cooling jacket and put in a jar containing the polluted water. The catalyst sheet has been supported in the solution with a glass holder at a controlled temperature of 25 °C during the experimental period. At different irradiation time intervals, samples of the irradiated water have been withdrawn for analysis using HPLC chromatograph with diode-array detector and $C_8$ column. The mobile phase has been acetonitrile/water (60:40) auto-injected at a rate of 1.0 ml/min.

## 3. Results and discussion

### 3.1. Structural and Microstructure studies

The deposited films are pure anatase and the texture of the films change with the increase of deposition temperature. This can be drawn from Fig. 1. The main anatase peak (101) diminishes and the (112) peak intensifies with the increase of deposition temperature. Also, the particle size has been calculated using Debye-Sherrer formula and presented in Table 1 [6].

Fig. 2 shows the morphology of the deposited films measured by SEM. All micrographs have been recorded at the same scale. As shown in the figure at the lowest temperature 250 °C large grains appear. Taylor et al. [11] reported similar results for films derived from

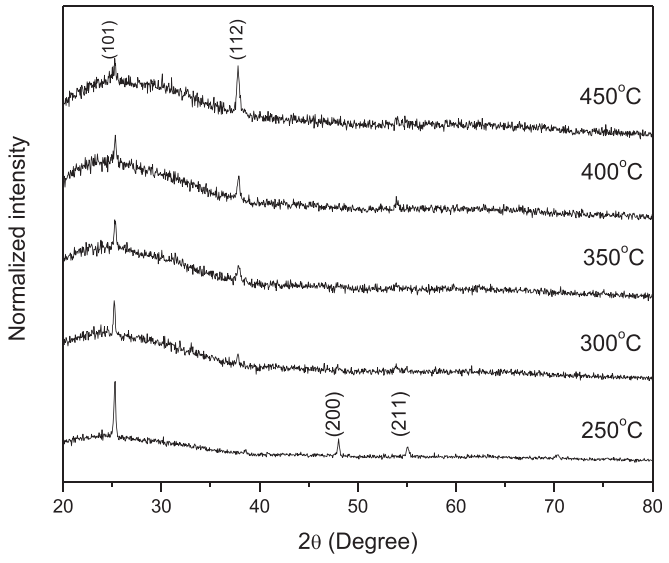


**Fig. 1.** Effect of deposition temperature on the crystallinity of $TiO_2$ thin films deposited at a) 250 °C, b) 300 °C, c) 350 °C, d) 400 °C and e) 450 °C.

**Table 1**
Thickness, crystallite size, and optical energy gap as a function of deposition temperature.

| Deposition temperature °C | Crystallite size (nm) | Thickness (nm) | Optical energy gap (eV) |
|---|---|---|---|
| 250 | 44.5 ± 1.7 | 286 ± 13 | 3.20 |
| 300 | 42.5 ± 0.8 | 317 ± 10 | 3.24 |
| 350 | 41.5 ± 1 | 336 ± 15 | 3.24 |
| 400 | 34.5 ± 2 | 245 ± 5 | 3.36 |
| 450 | 19.5 ± 1.5 | 234 ± 12 | 3.27 |

titanium nitrates at much more lower pressure. Moreover, they found that the entire substrate is covered by $TiO_2$ crystalline film at 159 °C. A decrease in the grain size with the increase in deposition temperature can be clearly seen especially at high temperatures. This result confirms the XRD results and agrees with data reported by Siriwongrungson et al. [16] using pulsed pressure MOCVD deposited films. As the deposition temperature increase the grains fragment into smaller oriented ones. The mean parameters affecting on the microstructure of thin films deposited by MOCVD are adsorption, desorption, reaction and diffusion of the precursor molecules. Deposition temperature has a crucial impact on these processes. At low temperatures the growth rate of films deposited by MOCVD is reaction limited. This happened in this study. For the films deposited at 250 °C and 300 °C the mean residence time of the precursor, the substrate coverage and the precursor diffusion are high. These processes drive the film to have large grains. But increasing the deposition temperature deteriorate them. So, as the temperature increases the diffusion length of the molecules decreases. This leads to an increase in the nucleation density which results in a separation between the grown grains. Scanning electron microscope results obtained by Shalini et al. [17] have shown smooth films in the temperature range from 400 °C to 525 °C. This might refer to the type of the used precursor and the small temperature scale investigated. Facets of 0.5 μm size have been observed by Zhang and Griffin [18]. This refers to the change of the reactor geometry and deposition pressure. The thickness of the films has been measured by cross sectional scanning electron microscope and presented in Table 1.

### 3.2. Optical properties

Transmittance spectra at different deposition temperatures are shown in Fig. 3. The transmittance of the films varies insignificantly with the increase in deposition temperature. Optical band gap can be calculated by using the formula;

$$(\alpha h\nu)^{1/2} = (h\nu - E_g)$$

where $\alpha$ is the absorption coefficient, h is Planck's constant $\nu$ is the frequency of incident light. The absorption coefficient has been calculated from [3];

$$\alpha = \frac{-\ln T}{d}$$

where T is the transmittance and d is the thickness. Fig. 4 shows the values of obtained energy gap. Table 1 summarizes the energy gap as a function of the deposition temperature.

`Zhang et al. deposited $TiO_2$ by photolytic CVD at substrate temperatures ranging from 200 °C to 350 °C and found a red shift in the transmittance and attributed it to the effect of the increase of deposition temperature but contrary to our results the crystallite sizes increased with the deposition temperature which may be due to the difference of the limiting parameters controlling the growth between the two studies [19]. Their calculated indirect band gap was 3.2 eV. Deshmukh et al. found the estimated direct band gap value converges to the same value with the increase of crystallite size due to raising deposition temperature of spray deposited samples [3]. The normal