Optical Properties of Lead Doped Titanium Oxide of Thin Films Prepared by Sol-Gel Method at Low Temperature

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Abstract The present paper reports on the structural and optical properties of undoped and 5% Pb-doped TiO2 thin films deposited on glass and silicon substrates prepared by the sol-gel technique have been investigated. Dip-coated thin films have been examined at different annealing temperatures (400-500 °C). The results shows that Pb-doped TiO2 thin films start to crystallize at low temperature (400 °C). The morphology and surface structure of the films were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) reveals a nanoporous structure of anatase and brookite with particle sizes ranging between 20 nm and 100 nm. Refractive index and porosity were calculated from the measured transmittance spectrum. SE study permits to determine the annealing temperature effect on the optical properties and the optical gap of the Pb-doped TiO2 thin films. Photoluminescence (PL) spectrum revealed that emission increase with annealing temperature. A slight shift of transmission curves to higher wavelengths is observed for curves of Pb-doped TiO2 thin films in comparison with those undoped, this was explained by the lowering of the band gap of TiO2.

Keywords Structural Properties, Optical Properties, Pb-doped TiO2, Thin Films, Sol-Gel

1. Introduction

Titania nanocrystalline films has been extensively studied because of its unique properties and wide verity of applications such as dielectric materials, planar waveguides, gas sensors, electrochromic systems, dye-sensitive solar cells and photocatalysts [1-4]. Titanium dioxide (TiO2) has been widely used because of its attractive properties; such as a the high band gap, transparent in the visible range, high refractive index, high dielectric constant, and ability to be easily doped with active ions. It is important to note that this material is non toxic with a high band gap semiconductor (3, 2 eV) insensitive to visible light and it absorbs in the near ultraviolet region [5]. TiO2 crystallizes in three polymorphic forms: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). The anatase phase has been reported to develop at temperatures below 800 °C, which at higher temperatures transforms to the more stable rutile phase. The occurrence of crystalline phase depends upon the deposition method, composition, density and annealing temperature. Legrand-Buscema et al. [6] reported that annealing the TiO2 films in 400-700°C temperature range exhibit anatase phase, however the annealing temperature beyond 800°C gives us a combination of rutile and anatase structure. The photocatalytic activity of TiO2 has been found to vary with its structural form and is reportedly higher in the anatase compared to the rutile [7, 8].

Additions of another semiconductor have been used to improve the properties of titanium dioxide. In principle, the coupling of different semiconductor oxides seems useful in order to achieve a higher photocatalytic activity [9]. Various composites formed by TiO2 and other inorganic oxides such as SiO2 [10], ZnO [11], MgO [12], ZrO2 [13], PbO [14,15], and so dopants like Fe, Zn, Au, Ag, Pb [16-20] have been reported. The above cited studies show that doping metal ions into TiO2 could extend the light absorption from UV to the visible region, leading to the improvement of the photon response of TiO2 by introducing additional energy levels within the band gap of TiO2. K.M. Krishna et al. have studied optical and structural properties of Pb-doped TiO2 thin films deposited by sol–gel dip coating technique. They have observed that the refractive index increases with increasing annealing temperature up to 500°C [21]. S.D. Cheng et al. have observed that Pb-doped TiO2 films prepared by sol–gel technique annealed at 500°C are highly transparent and
can support several waveguide modes. Up to date, there have been a number of studies on the preparation of Pb doped TiO$_2$ thin films [22]. Zeng et al. have prepared nanocrystalline lead titanate (Pb doped TiO$_2$) by an accelerated sol–gel process at 550°C [23]. Some lead titanate thin films are prepared at an annealing temperatures usually higher than 550°C [24], and sometimes in the temperatures range 650-800°C [25].

TiO$_2$ films have been prepared by many deposition techniques such as metal-organic chemical vapor deposition (MOCVD) [26], electron-beam evaporation [27], pulsed laser deposition [28] and reactive sputtering technique [29]. Among these methods, sol–gel technique is the simplest one and the less expensive (low power consumption), this process is generally used by dip coating or spin coating [30, 31]. Recently, Pb-doped TiO$_2$ thin films prepared by sol–gel method, exhibits many advantages like chemical stability, mechanical strength, high resistivity, high permittivity, these properties make this material a good candidate for use in the opto-electronic industry. However, Stiochiometric lead titanates have been prepared using sol-gel method by several authors with various precursors such as lead acetate trihydrate, Pb(CH$_3$COO)$_2$.3H$_2$O, and titanium tri-isopropoxide mono-acetylacetonate, Ti(C$_3$H$_7$O)$_4$(CH$_3$-COCHCOCH$_3$), which had been reported to give good stability and better control of viscosity [32-35]. M. Rahman et al. instead the lead nitrate, Pb(NO$_3$)$_2$ and titanium tetra-isopropoxide Ti(C$_3$H$_7$O)$_4$ as the source materials for Pb and Ti, respectively [36]. Studies of Pb-doped TiO$_2$ thin films have focused on their properties for use as optoelectronic devices such as solar cells, non-volatile memories [37, 38] and pyroelectric devices [39]. However, little attention has been paid on their applications in optical coatings at low temperature. Pb doped TiO$_2$ thin films has been successfully prepared in our laboratory by sol gel dip-coating using tetrabutyl-orthotitanate (C$_4$H$_9$O)$_4$ Ti and lead acetate trihydrate (C$_2$H$_3$O$_2$)Ti$_2$ as precursors.

This work is a continuation of our previous papers that has been done on structural, thermal and optical properties of undoped titanium oxide (TiO$_2$) reported by Bensaha [40, 41]. Further, Bensouyad et al. [11, 13] shows that the addition of 5% ZnO or 5% ZrO$_2$ in TiO$_2$ would be largely sufficient to crystallize the xerogels in anatase form by contrast to that of undoped TiO$_2$. However, thin films obtained from annealing at 350 °C crystallize in both anatase and brookite phases.

In this paper, we will report the effect of doping with Pb on structural and optical properties of TiO$_2$ thin films deposited by the sol–gel dip-coating process at low temperature. Several experimental techniques were used to characterize structural and optical properties resulting from different annealing treatments and different layer thicknesses: X-ray diffraction, Raman spectroscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Ellipsometry spectroscopy, UV–visible and photoluminescence spectroscopy.

## 2. Materials and Methods

### 2.1. Preparation of TiO$_2$ sol

The procedure of preparation includes the dissolution of 1 mol of butanol (C$_2$H$_4$OH) as solvent and 4 mol of acetic acid (C$_2$H$_4$O$_2$), 1 mol of distilled water is added as well as 1 mol of tetrabutyl-orthotitanate (C$_4$H$_9$O)$_4$Ti. In the second step, the solution of Pb was prepared from the dissolution of 1 mol of lead acetate (C$_2$H$_3$O$_2$)$_2$.3H$_2$O as precursor in 2 mol of acetic acid as catalyst. The concentration of the Pb ions is $x = 5\%$ at. $x$ which is defined as $x = [\text{Pb}/(\text{Ti} + \text{Pb})] \times 100$. Subsequently, 5 % at. Pb contained solutions was added into the TiO$_2$ sols.

### 2.2. Preparation of TiO$_2$ thin film

After stirring at room temperature for 24 h, the 5 % Pb-doped TiO$_2$ sols were dip-coated on cleaned and dried silicon and glass substrates (refractive index 1.517 and thickness of glass layers is 20 Å) with a dip-coating apparatus made in our laboratory. The substrates were dip-coated in the solutions at a constant rate of 6.25 cm s$^{-1}$. After each dipping, thin films were dried for 30 min at a distance of 40 cm from a 500 Wight source. The drying temperature of the light source is approximately equal to 100 °C. Subsequently, thin films were heat treated in the temperature range 400-500°C using a heating rate of 5°C min$^{-1}$ for 2 h in furnace.

### 2.2. Characterization

X-ray diffraction was performed by Siemens D5005 diffractometer, using a CuK$_\alpha$ radiation. The patterns were scanned at room temperature, over the angular range 10–70° 2h, with a step length of 0.1° 2h and counting time of 1 s step$^{-1}$. Raman spectra were recorded in a back scattering configuration using a Jobin Yvon micro Raman spectrometer coupled to a DX40 Olympus microscope. The samples of doped and undoped TiO$_2$ thin films were excited with a wavelength 532.8 nm with an output of 20 Mw. Optical properties of the films deposited on different (glass and silicon) substrates were examined by a U–VIS spectrophotometer (JASCO V-570). Morphological study was performed using scanning electron microscopy (SEM Philip XL-40 FEG) and atomic force microscopy (AFM) in tapping mode configuration by a Topometrix TMX 2000 Explorer AFM. Spectroscopic ellipsometry (SE) experiment was performed at room temperature using an automatic ellipsometer SOPRA GES5. The system uses a 75-W xenon lamp, a rotating polarizer, an autotracking analyser, a double monochromator, a photomultiplier tube and a GaInAs photodiode as...
detectors. Data were collected in the 0.25–1.5 µm region with the step of 0.005 µm, at incidence angle of θ = 70°. The photoluminescence (PL) measurements were carried out using the Jobin Yvon-Spxex make Spectrofluorometer (Fluorolog version-3; Model FL3-11) with 450W high-pressure xenon arc lamp as excitation source. PL excitation and emission spectra were acquired at room temperature for a spectral resolution of 0.2 nm and slit width of 0.25mm.

3. Results and discussion

3.1. Structural properties

3.1.1. Crystalline phases (XRD, Raman)

Fig.1 shows XRD pattern of both undoped and Pb-doped thin film obtained after 4 dippings and various annealing temperatures at 400, 450 and 500°C. Clearly, titanium oxide starts to crystallize at low temperature (400°C). Furthermore, all XRD pattern show a peak corresponding to (101) plane which is attributed to nanocrystalline of anatase whatever the annealing temperature. In addition to anatase phase, the presence of brookite can be observed, it crystallizes with (121) plane. However, K. M. Krishna et al find that the films have amorphous/nanocrystalline nature with the presence of pure anatase at 550°C and anatase-rutile mixture as the temperature increases to 850°C [21], but M.M. Rahman et al shows that the doped films with different concentration (5%, 10 % and 15 % Pb) have amorphous/nanocrystalline nature at 550°C [36]. Peak intensities corresponding to characteristic planes of anatase and brookite phases are obviously increased with the increase of annealing temperature. The latter is probably due not only to the increase of proportion of titanium oxide but also to the improvement of the crystalline quality.

![Figure1.](image)

**Figure1.** Evolution of diffraction patterns of 5 at. % Pb doped TiO₂ thin films; obtained at various annealing temperatures (400 °C (a), 450°C (b), 500°C (c)) for the same thickness

3.1.1.1. Surface morphology and grain size

The crystallite size D of TiO₂ thin films doped with Pb can be deduced from XRD line broadening using the Scherrer equation [42]:

\[
D = \frac{0.94 \times \lambda}{\Delta hkl - \Delta_{instr} \cos \theta}
\]

\[\text{where } \lambda \text{ is the wavelength of X-ray beam (Cu } K_{\alpha}=1.5406 \text{ Å), } \Delta hkl \text{ is the full width at half maximum (FWHM) of (hkl) diffraction peak, } \Delta_{instr} \text{ is the FWHM corresponding to the instrumental limit, and } \theta \text{ is the Bragg angle.}

The computed values of grain sizes, given in Table.1, were calculated for different temperatures of annealing with the same thickness. Thus, the obtained grain sizes for intense peaks of anatase and brookite increase from 16, 22 nm to 18, 53 nm and from 18, 22 to 20, 74 nm, respectively. In fact, as the annealing temperature increases the grain size also increase and doping with the Pb increases the crystallite size compared to the undoped one.

![Table1.](image)

**Table1.** Structural parameters of TiO₂ Thin Films Undoped and Doped with 5% at.Pb, for Different Annealing Temperatures.

| Phase       | L (nm) | (hkl) |
|-------------|--------|-------|
| **Undoped TiO₂** |       |       |
| Thin films  | 17.47  | (101) |
| Same thickness |       |       |
| **5% Pb doped TiO₂** |       |       |
| Thin films  | 18.02  | (101) |
| Same thickness |       |       |
| **Annealed at 400°C** |       |       |
| Anatase     | 18.42  | (101) |
| **Brookite** | 20.74  | (121) |
| **Annealed at 450°C** |       |       |
| Anatase     | 19.49  | (121) |
| **Brookite** | 20.74  | (121) |
| **Annealed at 500°C** |       |       |
| Anatase     | 19.53  | (121) |
| **Brookite** | 20.74  | (121) |

Fig.2 shows the Raman spectra in the range 100–900 cm⁻¹ of the Pb doped TiO₂ and undoped films grown on silicon substrates, annealed at the following temperatures 400, 450 and 500°C. The (a), (b), (c) and (d) spectra show symmetric vibration modes: A1g+2B1g +3Eg of tetragonal anatase phase identified at 144 cm⁻¹ (Eg), 197 cm⁻¹ (Eg), 397 cm⁻¹ (B1g), 435 cm⁻¹ (B1g), and 638 cm⁻¹ (Eg). The band positions are in good agreement with previous work for the anatase phase [43]. These bands can be assigned to anatase phase except the band 302 cm⁻¹, which is due to the crystallization of brookite phase. While the bands at 144, 197 and 638 cm⁻¹ can be assigned to both anatase and brookite phases [44, 45].

![Figure2.](image)

**Figure2.** Raman spectra of Pb doped TiO₂ and undoped films grown on silicon substrates, annealed at following temperatures 400, 450 and 500°C.
strong peak at 525 cm\(^{-1}\) corresponding to the LO-phonon mode of Si (1 0 0) was observed in all measurements. It can be seen that the intense Raman peak corresponding to the \(E_g\) mode of TiO\(_2\) shifted towards higher wavenumbers. This shift can be attributed to the quantum confinement effect of TiO\(_2\) nanoparticles [46, 47]. No other peaks corresponding to doped samples have been observed in the spectra, which confirm the XRD results.

The absence of the characteristic lead vibration modes in the Raman spectra reveals that there is no segregation of that material into TiO\(_2\). This indicates that doping with lead may occupy the substitutional sites in the host lattice.

### Figure 2

Raman Spectrum of 5 % at. Pb doped TiO\(_2\) Thin Films Annealing at Various Temperatures: (400°C (a), 450°C(b), 500°C(c)); A = anatase, Si = substrate

#### 3.1.2. Surface morphology

SEM micrographs, Fig. 3 undoped and doped TiO\(_2\) Fig. 3 (a-c) show the surface morphology of pure and Pb-doped TiO\(_2\) thin films deposited at various temperatures. These micrographs reveal the nanocrystalline nanoporous morphology with a certain degree of agglomeration and an average particle size ranging from 20 to 100 nm. Also, an increase in crystal size and crystallization of the films has been observed with increasing temperature, which is in agreement with XRD results. At the initial stages, the grain shape is spherical, but as the annealing temperature increases, crystallization with crystals of clear elongated needle-shape have been observed (micrograph (c) for 500°C). This is due to an increase in surface mobility with increasing temperature, thus allowing the films to lower its total energy by growth of grains and decrease of grain boundary area. Moreover, as the temperature increases, the presence of two kinds (small and bulky) of crystallites were noticed (micrograph (b) for both 450°C and (c) 500°C), which further supports the existence of mixed phases as also envisaged by XRD analysis (pattern (b) and (c) for both 450°C and 500°C in Fig. 1).

### Figure 3

SEM Surface Morphology Images of the TiO\(_2\) Thin Films Undoped and Doped with Pb (a-c) Obtained at Various Annealing Temperature: (a) 400°C, (b) 450°C, (c) 500°C.
AFM surface imaging analysis investigation confirmed the crystallization of the films due to annealing temperature. It can be observed from Fig. 4 (a, b, c) a large spherical grain more uniform are display not only at the surface morphology but are distributed along the thickness of the film; however, as the annealing temperature increased the grains tend to agglomerate in preferred orientation. The computed values of microstructural parameters, given in Table 2, were calculated for different temperatures of annealing with the same thickness. Thus, increasing the annealing temperature from 400 to 500 °C increase slowly the surface roughness RMS (Root Mean Square) from 1.05 to 2.67 nm respectively. On the other hand, the grain sizes are ranged from 20.05 to 100.1 nm. The increase in the roughness is due to the increase in the grain size. The well-defined crystallinity and particle size of doped TiO₂ was confirmed by the good correlation with XRD and SEM analysis.

![AFM images of the TiO2 thin films doped with Pb obtained at various annealing temperature: (a) 400°C, (b) 450°C, (c) 500°C.](image)

**Table 2.** The influence of the annealing temperature on Pb-doped TiO₂ film average grain size, roughness and optical band gap obtained by reflectance and SE analyses.

| T(°C) | AFM analysis | UV–vis analysis | SE analysis |
|-------|--------------|-----------------|-------------|
|       | Average grain size (nm) | RMS (nm) | Optical band gap (eV) | Optical band gap (eV) |
| 400   | 20.05         | 1.05            | 2.59        | 2.60           |
| 450   | 27.98         | 1.82            | 2.48        | 2.38           |
| 500   | 100.1         | 2.67            | 2.01        | 1.98           |
3.2. Optical properties

3.2.1. UV absorption analysis

Fig.5 displays diffused scattering UV–VIS transmittance spectra of undoped and Pb-doped TiO2 thin films, for different annealing temperatures and different dipping numbers in the wavelength range 300–800 nm. Transmission of titanium oxide thin films decreases with the increase of annealing temperature and with the number of dipping. Optical transmittance higher than 95% in the visible region of spectrum is obtained for all films. The transmission of the titanium oxide thin films in the visible region, increase with the Pb doped. This can be ascribed to the formation of larger particles on the surface of Pb-doped TiO2 thin films [48].

The bands caused by the interference color of the film appeared in the wavelength range of 350–800 nm. The amplitude of interference spectra also increases with increasing annealing temperature and number of dipping, due to the increase in the refractive index of thin films. A slight shift of transmission curves to higher wavelengths is observed for curves of doped thin films (Fig.5) in comparison with those undoped.

The refractive index of TiO2 thin films was calculated from measured UV–VIS transmittance spectrum. Evaluation method used in this work is based on the analysis of UV–VIS transmittance spectrum of a weakly absorbing film deposited on a non-absorbing substrate. The refractive index \( n(\lambda) \) over the spectral range is calculated by using the envelopes that are fitted to the measured extreme [49]:

\[
    n(\lambda) = \sqrt{s + \sqrt{s^2 - n_0^2(\lambda)n_s^2(\lambda)}} \quad (B.2)
\]

\[
    s = \frac{1}{2}(n_0^2(\lambda) + n_s^2(\lambda) + 2n_0 n_s T_{\text{max}}(\lambda) - T_{\text{min}}(\lambda)) \times \frac{T_{\text{max}}(\lambda)}{T_{\text{min}}(\lambda)} \quad (C.3)
\]

Where \( n_0 \) is the refractive index of air, \( n_s \) is the refractive index of the film, \( T_{\text{max}} \) is the maximum envelope, and \( T_{\text{min}} \) is the minimum envelope. The thickness of the films was adjusted to provide the best fits to the measured spectra. In this study, all the deposited films are assumed to be homogeneous. The porosity of the thin films is calculated using the following equation [50]:

\[
    \rho = \left(1 - \frac{n^2}{n_d^2} - 1\right) \times 100(\%) \quad (D.4)
\]

Where \( n_d \) is refractive index of pore-free anatase \((n_d=2.52)\) [51], and \( n \) is the refractive index of porous thin films. The results of the computed refractive index \((n)\) and porosity \((\rho)\) are reported in Table.3. It is noted that the refractive index of thin films of doped titanium oxide increases with increasing annealing temperature and number of dipping, the porosity decreases. The increase in refractive index with annealing temperature is due to densification of the film [52]. Moreover, this results correlated to phase transition (anatase, anatase–brookite), which increases grain sizes and/or pore destruction in films due to the increase of annealing temperature and number of dipping [11, 40].

| Ti(°C) | 4 Layers | 6 Layers | 8 Layers |
|--------|----------|----------|----------|
| 400    | 2,27     | 12,37    | 2,49     | 1,48     | 2,67     | 9,40     |
| 450    | 2,59     | 3,46     | 2,55     | 1,49     | 2,65     | 6,43     |
| 500    | 2,63     | 5,44     | 2,64     | 5,94     | 2,71     | 7,42     |

Table.3. Variation of Refractive Index \((n)\) and Porosity \((\rho)\) for Different Annealing Temperatures and Different Number of Layers.

Figure 5. Transmittance Spectra of Thin Films TiO2 undoped and Doped with Pb Thin Films for Different Annealing Temperature (400-500°C).
3.2.3. Spectroscopic Ellipsometry

Fig. 7 (a) and (b) show the results of the ellipsometric analysis in terms of refractive index (n) and extinction coefficient (k), as a function of wavelength (300-1000 nm), for 5 at.% Pb doped TiO_2 samples annealed at 400, 450 and 500°C for 2 hours. It can be clearly seen that the refractive index of the Pb doped TiO_2 thin films increases with increasing annealing temperature and wavelength. Whereas, S.K. Sharma et al. [54] reported that the refractive index decreased with the increase of wavelength and annealing temperature. In Table 2 we listed the SE obtained Eg values; the optical band gap is in good agreement with the reflectance results. As can be seen, we can confirm using another optical technique (SE) that the annealing affects the optical band gap, which is found to decrease by increasing the temperature from 2.60 eV to 1.98 eV. These can be explaining by effect of Pb dopant in TiO_2 thin film compared with the undoped TiO_2 [40]. Theoretical Krishna et al. [21] reveals that we can reduce the band gap of TiO_2 by doping with Pb. These results are consistent with the reflectance results. The ellipsometric analysis also allows as well finding the layer thicknesses of Pb doped TiO_2 samples. The thicknesses change from 117.3 nm to 511.1 nm for the sample annealed between 400°C and 500°C for 2 hours.

3.2.4. Photoluminescence spectroscopy

Fig. 8 shows Photoluminescence (PL) spectra of Pb-doped TiO_2 thin films, annealed at different temperatures (400°C, 450°C and 500°C). An intense greenish yellow luminescence is observed in the visible region, and doping with 5 at. % of lead increases peak intensity. PL spectra of our samples exhibits three peaks at 405 nm, 430 nm, and 480 nm, demonstrating that the lead as a dopant give rise to new PL phenomena.
peak at 430 nm can be seen. It is ascribed well to the transitions to the $^1P_1$ level of Pb ions, the doping with Pb introduction a new defect sites in TiO$_2$ that enhance non-radiative recombination of the excited electrons [57]. The prominent peak at 480 nm can be attributed to the oxygen vacancies. Addition of Pb shifts the peak intense towards to higher wavelengths (lower energy), further supports to the lowering of the band gap of TiO$_2$ with Pb doping. Also, the PL emission intensity deduces a continuous increase in the luminescence intensity as the temperature increases. The increase in emission intensity with annealing temperature may be due to the presence of mixed phase at high temperatures, which confirmed by XRD and SEM analyses.

4. Conclusions

In this study, structural and optical properties of Pb-doped TiO$_2$ thin films, prepared by sol–gel method using dip-coating technique were studied which were successfully prepared on glass and silicon substrates. XRD and Raman spectroscopy results show that doped thin films crystallize in both anatase and brookite phases. The crystallite size has been increased with increasing of annealing temperature from 400 to 500°C. SEM and AFM observations of doped thin films reveal nanoporous structure with crystallite size in the range of 20 nm to 100 nm in comparison with those undoped. Analysis of UV–VIS transmission spectra shows that the doped thin films are transparent in the visible range and opaque in the UV region. The complex index and the optical band gap ($E_g$) of the films were determined by the spectroscopic ellipsometry analysis. We have found that spectroscopic ellipsometry and reflectance are in good agreement. The refractive index increases with increasing the annealing temperature and wavelength. While, the porosity decreases, energy band gap of Pb-doped TiO$_2$ films decrease owing to an increase in annealing temperatures. PL measurement shows also a high emission with a slight shift to higher wavelengths (lower energy), which supports the lowering of the band gap of Pb-doped TiO$_2$. In this study, we have carefully prepared optical materials of 5 % Pb-doped TiO$_2$ thin films.

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