Effect of Doping Lead on Optical and Structural Properties of Thin Films of TiO_2

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Abstract:

The present paper reports on the structural and optical properties of 5% Pb-doped TiO_2 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 TiO_2 thin films start to crystallize at low temperature (400 °C). The morphology and surface structure of the films were studied by SEM reveals a nanoporous structure of anatase with particle sizes ranging between 20 nm and 100 nm. UV-visible and SE spectroscopy study permits to determine the annealing temperature effect on the optical properties and the optical gap of the TiO_2 doped Pb thin films. These results improve that the properties of thin films of TiO_2 enhanced by lead doping which increase the photo activity of films.

Keywords: Structural Properties; Optical Properties; Pb-doped TiO_2; Thin Films; Sol-Gel.

1. Introduction

Titanium dioxide also known 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 (TiO_2) 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]. The occurrence of crystalline phase depends upon the deposition method, composition, density and annealing temperature. Legrand-Buscema et al. [6] reported that annealing the TiO_2 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 TiO_2 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]. The above cited studies show that doping metal ions into TiO_2 could extend the light absorption from UV to the visible region, leading to the improvement of the photon response of TiO_2 by introducing additional energy levels within the band gap of TiO_2. K.M. Krishna et al. have studied optical and structural properties of Pb-doped TiO_2 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 [10]. S.D. Cheng et al. have observed that Pb-doped TiO_2 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 [11]. Zeng et al. have prepared nanocrystalline lead titanate (Pb doped TiO_2) by an accelerated sol–gel process at 550°C [12]. Some lead titanate thin films are prepared at an annealing temperatures usually higher than 550°C [13], and sometimes in the temperatures range 650-800°C [14].

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, 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 $(C_4H_9O)_4Ti$ and lead acetate trihydrate $(C_2H_3O_2)_2.3H_2O$) as precursors.

In this paper, we will report the effect of doping with lead 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), Ellipsometry spectroscopy (SE), UV-visible spectroscopy.

2. Experimental

2.1. Preparation of TiO_2 sol

The procedure of preparation includes the dissolution of 1 mol of butanol (C_4H_9OH) as solvent and 4 mol of acetic acid ($C_2H_4O_2$), 1 mol of distilled water is added as well as 1 mol of tetrabutyl-orthotitanate $(C_4H_9O)_4Ti$. In the second step, the solution of Pb was prepared from the dissolution of 1 mol of lead acetate $(C_2H_3O_2)_2+3H_2O$) as precursor in 2 mol of acetic acid as catalyst. The concentration of the Pb ions is x = 5 % at., which is defined as x = [Pb/ (Ti + Pb)] x 100. Subsequently, 5 % at.of Pb contained solutions was added into the TiO_2 sols. 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 and heat treated in the temperature range 400-500°C using a heating rate of 5°C min^{-1} for 2 h in furnace.

3. Results and discussion

3.1. Structural properties

3.1.1. Crystalline phases (XRD, Raman)

Figure.1 shows XRD pattern of Pb-doped thin film obtained after 4 dippings and various annealing temperatures at 400, 450 and 500°C. All XRD pattern show an amorphous/nanocrystalline structure which attributed to nanocrystalline of anatase structure whatever the annealing temperature. Up to an annealing temperature 500°C, it can be observed that the films changed from amorphous to nanocrystalline as anatase phase with peaks existence at (101),(111),(112), (105) and (200) plans. However, K. M. Krishna et al find that 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 [10], 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 [15]. The peak intensity increase and became sharper with increased of annealing temperature, indicating better crystallization. In XRD patterns there is no trace of lead oxide (PbO) was observed in films crystallized, the absences of PbO means that the amount of Pb is indeed doped in TiO_2 lattice.

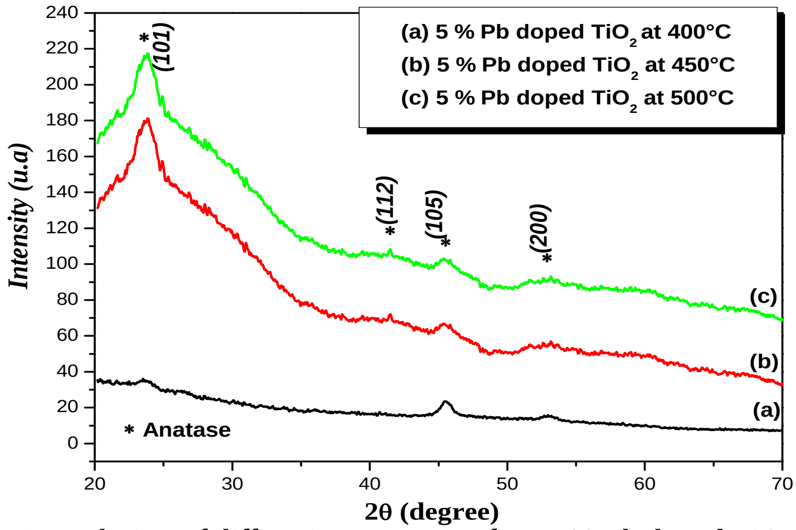


Figure.1. *Evolution of diffraction patterns of 5 at. % Pb doped TiO_2 thin films; obtained at various annealing temperatures (400 °C (a), 450°C (b), 500°C (c)) for the same thickness.*

Figure.2 show the Raman spectra of the Pb doped TiO_2 thin films grown on silicon substrates, annealed at the following temperatures 400, 450 and 500°C. The (a), (b) and (c) spectra show symmetric vibration modes of anatase phase identified at: 144 cm^{-1}, 197 cm^{-1}, 397 cm^{-1}, 435 cm^{-1}, and 638 cm^{-1} [16]. These bands can be attributed to anatase phase except the band at 302 cm^{-1} and 520 cm^{-1} which corresponding to vibration mode of Si (1 0 0) substrate. It can be seen from Fig.2 that the intense Raman peaks shifted towards higher wavenumbers (bleu shift). In Raman spectra there is no peaks associating to lead dopant have been observed, which may be explained by no segregation of these materials on TiO_2 lattice. We think that the Pb^{2+} ions may be occupy the vacancy sites by entering into the crystal lattice of TiO_2 through the substitional mode.

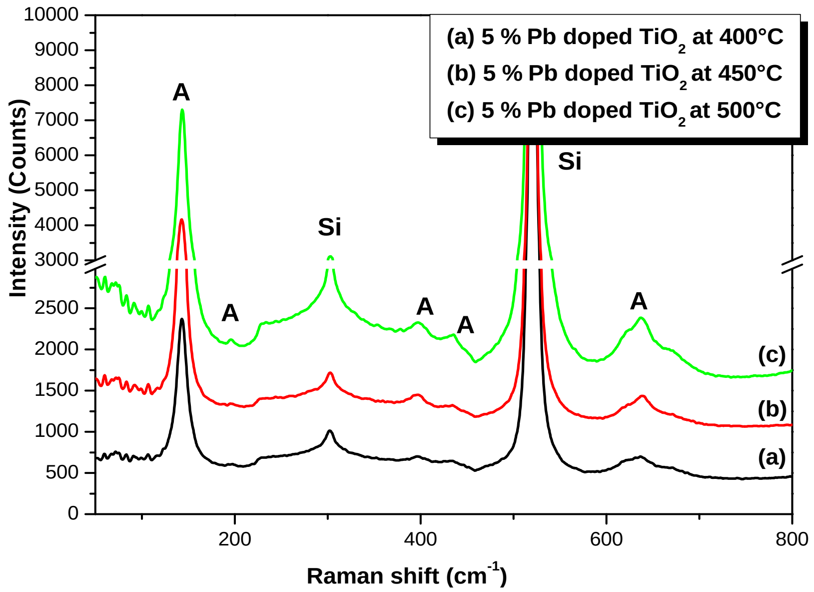
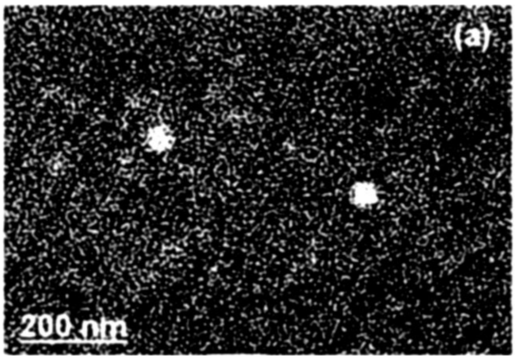


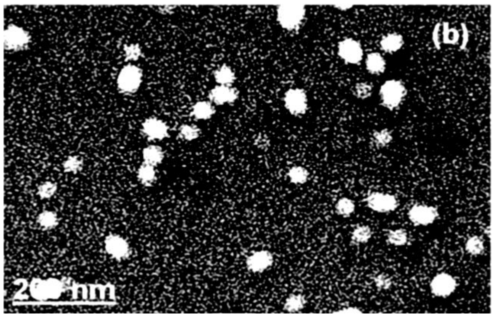
Figure.2. *Raman spectrum of 5 at.% Pb doped TiO_2 thin films annealing at various temperatures : (400°C (a),450°C(b),500°C(c)); A = anatase,Si = substrate.*

3.1.2. Surface morphology

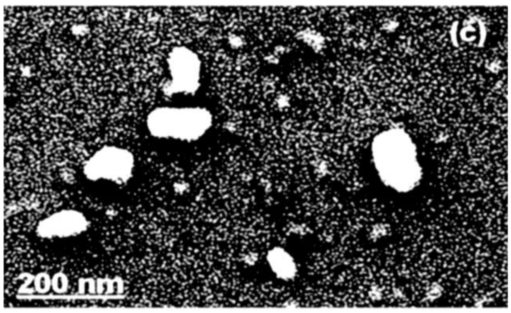
SEM micrographs, figure.3 (a-c) show the surface morphology of Pb-doped TiO_2 thin films deposited at various temperatures. These micrographs reveal the nanocrystalline nanoporous morphology of anatase structure with certain degree of agglomeration and an average particle size ranging from 20 to 100 nm. Also, an increase in crystal size and crystallization of the films has been observed with increasing temperature. 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 (see micrograph (c) 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 of crystallites was noticed (small micrograph (b) for 450°C and large (micrograph (c) 500°C). These results also are in good agreement with XRD analysis.



(a) 400°C



(b) 450°C



(c) 500°C

Figure.3. (a-c) *SEM surface morphology images of the TiO_2 thin films doped with Pb obtained at various annealing temperature: (a) 400°C, (b) 450°C, (c) 500°C.*

3.2. Optical properties
3.2.1. UV absorption analysis

The UV–VIS transmittance spectra of Pb-doped TiO_2 thin films on glass substrates for different annealing temperatures (400-500°C) having thickness 100 nm and 500 nm in wavelength range of 300-800 nm are shown in Figure.4. All spectrums of the optical transmission show that the amplitude transparency of the titanium oxide doped with lead thin films are between 60-90 % in the visible region, and this transparency apparently decreases with increasing of annealing temperature, this may be explain by the increase of crystalline ratio on the surface of Pb-doped TiO_2 thin films. Moreover, it can be observed from the films bands of interference color, due to the increase in the refractive index of thin films. It is clearly that the doped curves were marked by "bleu shift" to higher wavelengths compared with undoped one. This is owing to the absorption edge of anatase phase, which has a higher band gap (3, 65 eV).

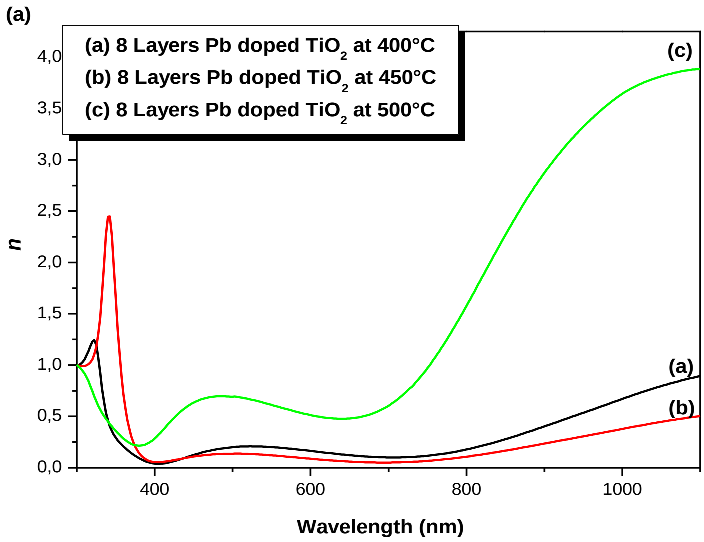


Figure.4. *Transmittance spectra of thin films pure TiO_2 and doped with Pb thin films for different annealing temperature (400-500°C).*

3.2.2. Refractive index (n) and extinction coefficient (k)

The ellipsometric analysis (SE) results of the refractive index (n) and extinction coefficient (k) of Pb-doped TiO_2 thin films annealed at 400, 450 and 500°C, as a function of wavelength (300-1000 nm) are show in Figure.5 (a) and (b). It can be clearly see that the refractive index (n) and extinction coefficient (k) of the Pb doped TiO_2 thin films increases with increasing annealing temperature and wavelength, whereas, S.K. Sharma et al. [17] reported that the refractive index decreased with the increase of wavelength. These experimental results confirmed with the theoretical study doing by Krishna et al. [10] they reveal that the TiO_2 band gap can reduce by lead (Pb^{2+}) doping.

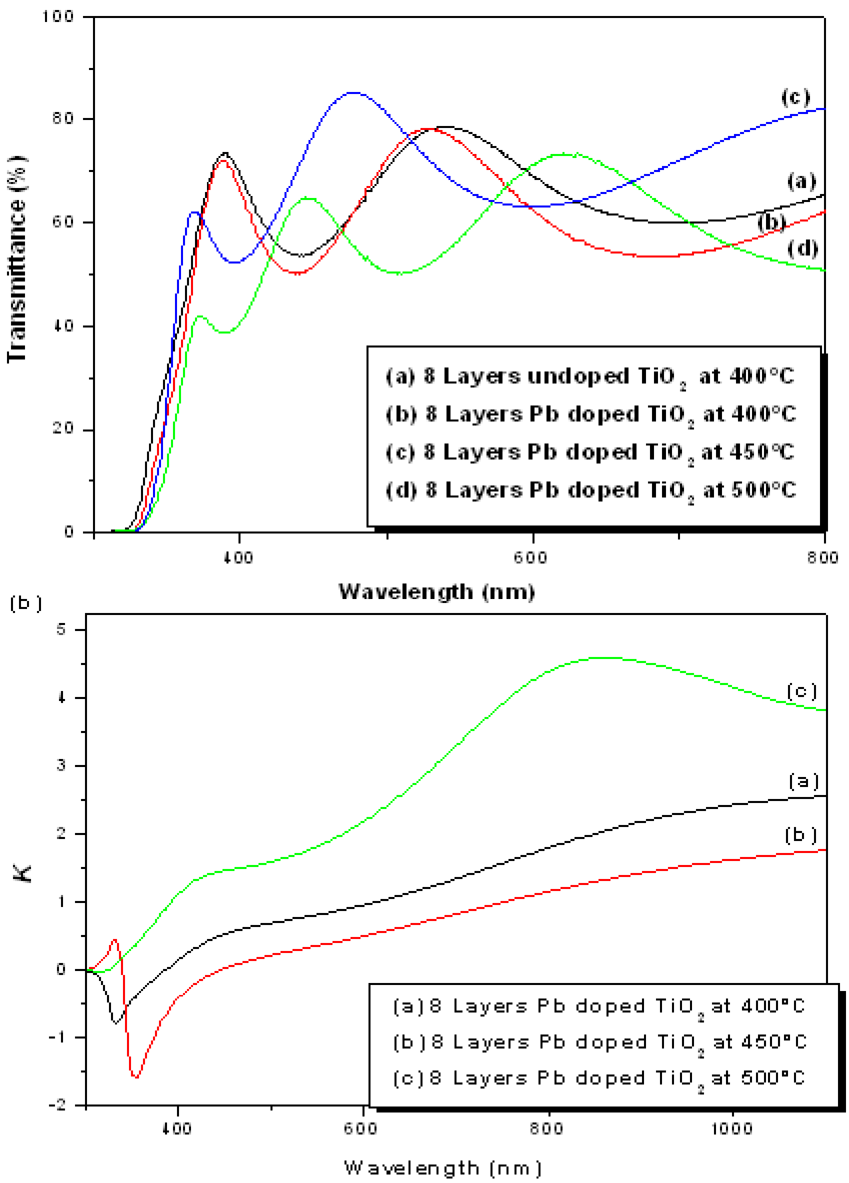


Figure.5. *Refractive index (a) and extinction coefficient(b) as a function of wavelength of Pb doped TiO_2 films annealed at 400°C, 450°C and 500°C.*

4. Conclusion

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 anatase phase. The crystallite size has been increased with increasing of annealing temperature from 400 to 500°C. SEM observations of doped thin films reveal nanoporous structure with crystallite size in the range of 20 nm to 100 nm. 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 UV-visible results are in good agreement. The refractive index increases with increasing the annealing temperature and wavelength. While, the energy band gap of Pb-doped TiO_2 films decrease owing to an increase in annealing temperatures. In this study; we have carefully prepared optical materials of 5 % Pb-doped TiO_2 thin films.

5. References

[1] Hara K, Hariguchi T, Kinoshita T, Sayama K, Arakawa H ,J Sol Energy Mater 70,151(2001).

[2] R. Mechiakh, F. Meriche, R. Kremer, B. Boudine, A. Boudrioua, Opt. Mater.30, 645(2007).

[3] Natarajan C, Nogami G ,J Electrochem Soc 143,1547(1996).

[4] Yu J, Zhao X, Zhao Q ,J Mater Chem Phys 69,25(2001).

[5] Y. Paz, A. Heller, J. Mater. Res. 12,2759(1997).

[6] C. Legrand-Buscema, C. Malibert, S. Bach, Thin Solid Films 418,79(2002).

[7] S.-J. Tsai, S. Cheng, , Catal. Today 33,227(1997).

[8] H.P. Maruska, A.K. Ghosh , Sol. Energy 20,443(1978).

[9] Wang C, Xu BQ, Wang XM, Zhao JC,J Solid State Chem 178,3500(2005).

[10] K. M. Krishna, Md. M-ur-Rahman, T.Miki, T. Soga, K. Igarashi, S. Tanemura , M. Umeno. Applied Surface Science 113 /114 ,149-154(1997).

[11] S.D. Cheng, C.H. Kam, Y. Zhou, W.X. Que, Y.L. Lam, Y.C. Chan, W.S. Ganb 245. Thin Solid Films 375,109-113(2000).

[12] X. Zeng, Y.Liu, X. Wang, W. Yin, L. Wang, H. Guo, Materials Chemistry and Physics 77,209–214(2002).

[13] R. Thomas, D.C. Dube, Jpn. J. Appl. Phys. Pt.136,7337(1997).

[14] C.J. Lu, H.M. Shen, J.S. Zhu, Y.N. Wang, J. Phys. D: Appl. Phys. 30,2338(1997).

[15] M.M. Rahman, T. Miki, K.M. Krishna, T. Soga, K. Igarashi, S.Tanemura, M. Umeno, Mater. Sci. Eng. B41,67(1996).

[16] M.Z. Hu, P. Lai, M.S. Bhuiya, C. Tsouris, B. Gu, M. Paranthaman, J. Gabitto, L. Harrison, J. Mater. Sci. 44,2820–2827(2009).

[17] S.K. Sharma, M. Vishwas, K.N. Rao, S. Mohan, D.S. Reddy, K.V.A. Gowda, J. Alloys. Compd. 471,244(2009).