OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 5, No. 9, September 2011, p. 960 - 963

Optoelectronic properties and band gap narrowing in chemically PbO doped TiO_2 thin film

E. C. EKUMA*, E. V. ESABUNOR, E. OSAROLUBE, I. O. OWATE, F. I. EZEMA[a], E. O. CHUKWUOCHA,
M. C. ONYEAJU
Department of Physics, University of Port Harcourt, Rivers, Nigeria
[a]*Department of Physics and Astronomy, University of Nigeria, Nigeria*

Films of PbO doped TiO_2 have been deposited on the pores of polyvinylpyrrolidone (PVP) matrix at temperature of $70^{o}C$ using chemical bath deposition technique. The films were annealed at temperature of 250°C at varying molar concentration of $Pb(CH_3COO)_2.3H_2O$; and then characterized using UNICO UV-2102 PC. The films show that there is significant band gap narrowing (E_g is in the range 1.34 to 1.61 eV) towards the absorption edge of the visible light region. The Rutherford – Backscattering shows a thickness of 450 nm and the elemental composition of the film stiochiometric as $Ti_{0.156}O_{0.758}Pb_{0.086}$. The optoelectronic properties of the film studied show that it can be harnessed for possible application as window material in the entire VIS region; and especially for harvesting solar radiation and photocatalysis.

(Received May 13, 2011; accepted September 15, 2011)

Keywords: Solar cells, Optoelectronic, Band gap narrowing, Characterization, Doped titanium, Photocatalysis

1. Introduction

The development of advanced materials for alternative and sustainable energy applications is an extremely active research area of great importance. In particular, much effort has been devoted to searching for new catalytic materials that can readily split water to generate hydrogen as an environmentally friendly fuel via photolysis using the abundant energy from sunlight [1]. Titanium dioxide (TiO_2) is one of the promising materials that suit these conditions. TiO_2 is not just a better photocatalysts in heterogeneous photocatalytic applications [2] because of its functionality, but also a promising material for photochemical applications [3]. The diverse advantages and promising applications offered by TiO_2 are numerous. They includes but not limited to: 1) photocatalysis of poisonous compounds [4]; 5) One of its current usages is in the photocatalytic oxidation (PCO) to break down and destroy many types of organic pollutants [4]; 6) It has been used to purify drinking water, destroy bacteria and viruses, remove metals from waste streams, and breakdown organics into simpler components of water and CO_2 [4-8].

With regards to the photoreaction efficiency capabilities of TiO_2, it is severely limited by its large intrinsic band gap (3.0eV) which, only absorbs in the ultraviolet region of the electromagnetic spectrum [6], with only about 3% of the more abundant and important visible spectrum absorbed [2]. The effective utilization of visible light occupying the main part of the solar spectrum has been one of the important reasons for the increased study of optoelectronic properties of TiO_2. The most vital prerequisite for the enhancement of the solar energy conversion efficiency of TiO_2 is to harness it to absorb more in the visible region by methodically narrowing the band gap below 2.0 eV.

In this study, we report on the successful chemical deposition and characterization of transparent TiO_2 doped with PbO thin films on soda – lime silica glass (SLSG) substrates on the pores of polyvinylpyrrolidone (PVP) matrix at varying molar concentrations of $Pb(CH_3COO)_2.3H_2O$.

2. Experimental procedure

Preparation of Solutions: All the chemicals used were of analytical grade and all the solutions were prepared in doubly distilled water.

Standard $TiCl_3$ solutions were prepared from its stock solution. 1M NaOH solution was prepared by dissolving 4g of its pellets in 100ml of distilled water. Gelatin (G-8) solution was prepared by dissolving 1.5gm of insoluble G-8 in 250ml of distilled water and stirred using magnetic stirrer to obtain a homogenous solution. Also, polyvinylpyrrolidone (PVP) solution was prepared by adding 4g of it to 400 ml of distilled water. The mixture was initially insoluble but becomes soluble when stirred by a magnetic stirrer. Also, 1M, 0.7M, 0.5M, 0.25M and 0.1M Lead Acetate solutions were prepared by dissolving 37.93g, 26.55g, 18.96g, 9.48g and 3.79g respectively of lead acetate in 100ml of distilled water .

Experimentation: The soda – lime – silica glass substrates were initially degreased in HCl for 24h, washed with mild soap, rinsed in water, cleaned with acetone and dried in open air. The deposition process was of two stages. 1) The initial deposition of TiO_2: The reaction bath contained 1M 5ml $TiCl_3$; 1M 3ml NaOH and 38 ml gelatin which were carefully added in that order. The content of the bath was stirred to obtain a colorless homogenous mixture and substrate allowed in the reaction bath for 7h at 70^{o}C. 2) The reaction bath contained 0.1M (sample **E**), 0.25M (sample **F**), and 0.50M (sample **G**) each of 10mL $Pb(CH_3COO)_2.3H_2O$; 40mL PVP and 6mL NH_3 were added in that order, stirred to give a colorless mixture. The substrates from first phase were carefully immersed into the reaction baths for 7h, and the temperature maintained at 70^{o}C.

The slides were carefully removed from the bath, rinsed in distilled water and allowed to dry in open air. These samples were later annealed at temperature range of 250^{o}C for 1h and then characterization for the optical and solid state properties. The normal incidence transmittance and absorbance spectrum of the deposited films were characterized using UNICO UV-2102 PC spectrophotometer in the UV – VIS – NIR region; and measurements were taken under the parametric conditions of normal incident, ambient temperature and uncoated microscopic glass slide used as blank. The Rutherford Back – Scattering (RBS) characterization were also carried out to determine the Stoichiometry of the film.

RBS Measurement: The composition of the samples was determined by RBS using a Van de Graaff accelerator. A 2.20 MeV, 3.00 μC at 2.20 nA $^4He^+$ ion beam at normal incidence was used, and backscattered particles were detected at 170^o, with the number of atoms per surface unit area (areal density) determined by computer simulation.. The method adopted in the analysis of the RBS is similar to that, which has been extensively described elsewhere [see 9,10].

3. Results and discussion

The results of the various optoelectronic properties of the developed films were as shown in Figs. 1 – 6.

Optoelectronic analysis: The plot of the optical absorbance as a function of wavelength can be inferred from Fig. 1. It showed gradual decrease along the UV – VIR – NIR spectrum for all the samples being studied. On the contrary, the transmittance as a function of wavelength increased throughout the same electromagnetic spectrum, however, as it can be seen (see Fig. 2), that of sample 0.1M $Pb(CH_3COO)_2.3H_2O$ is almost constant throughout. The inference that can be made from this is that lower concentration of $Pb(CH_3COO)_2.3H_2O$ generally lowers the optical transmittance of the films.

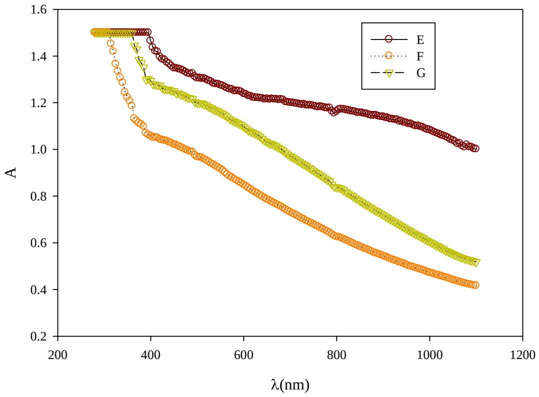

Fig. 1. The graph of Absorbance (A) as a function of wavelength (λ) for TiO_2 - PbO thin films.

The Reflectance as a function of wavelength (Fig. 3) and the Absorption coefficient as a function of photon energy (Fig. 4) all increased gradually in the entire "em" spectrum being studied. Critical look also shows that the concentration of $Pb(CH_3COO)_2.3H_2O$ is a major determinant factor. The variation of the spectra transmittance (*T %)* and reflectance (*R %)* with the photon wavelength are as shown in Figs. 2 and 3 respectively. All samples showed a slight transmittance (2 - 10%) in the UV region but a high transmittance in the NIR- VIS region (10 - 40%), especially in the case of sample **F**. Conversely, the reflectance of the film is found to be low (0 - 20.5%) within the same region. The high transmittances of the films may be attributed to the small particle size which reduces light scattering [2]. Critical analysis of these spectra, indicate that it is obvious that the films present relatively high optical quality, with an absorption in the visible region that is characterized by the typical interference pattern found when a transparent thin film is deposited onto a substrate of varying index of refraction. The observed high transmittance and low reflectance exhibited by the film makes it useful for solar thermal application in flat plate collectors, fabrication of antireflective coating materials.

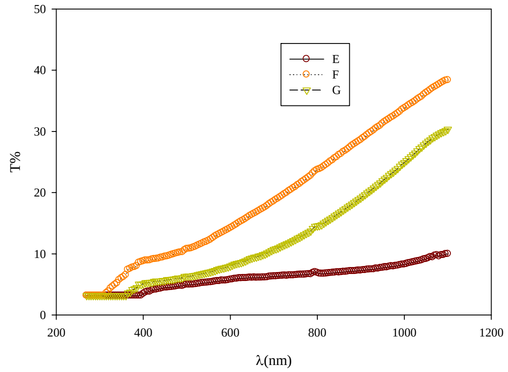

Fig. 2. The graph of Transmittance (T) as a function of wavelength (λ) for TiO_2 - PbO thin films.

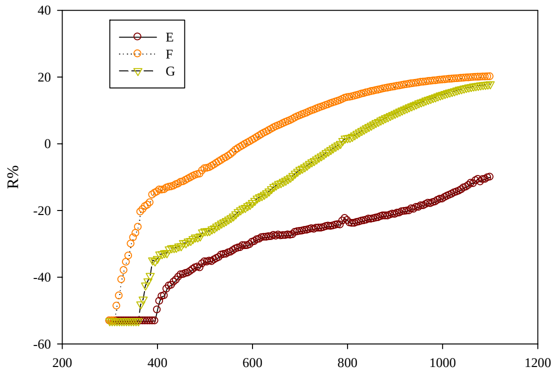

Fig. 3. The graph of Reflectance (R) as a function of wavelength (λ) for TiO_2 - PbO thin films.

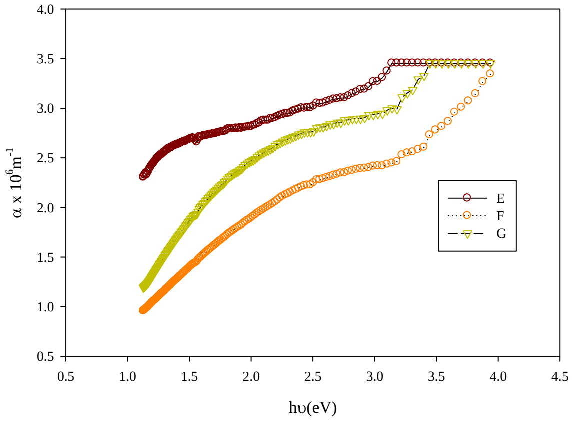

Fig. 4. The graph of Absorption coefficient as a function of Photon energy for TiO_2 - PbO thin films.

From Fig. 5, it can be inferred that the synthesized samples show direct band gap with an optical band gap values of 1.34 eV for sample E, 1.61 eV for sample F and 1.50 eV for sample G. Observe that the band shifts are: 0.27 eV and 0.11eV in that order. Observe that the energy gaps were significantly affected by the varying concentration of $Pb(CH_3COO)_2.3H_2O$, as can be inferred from the band gap shifts. The use of TiO_2 as one of the most promising photocatalysts for solar energy utilization and environmental cleanup has been hampered by its large intrinsic band gap (3.0 eV), leading to reduction in its photoreaction efficiency. However, as can be inferred from the optical properties of the studies films and their corresponding band gap values, there is significant narrowing of the band gap of pure titanium oxide by doping it with PbO to well below 2eV where it becomes useful in the optical region of the electromagnetic spectrum. Also, since the photocatalysis of water occurs at band gap in the range of less than 2 eV, no doubt, this material is a possible candidate for this very important application.

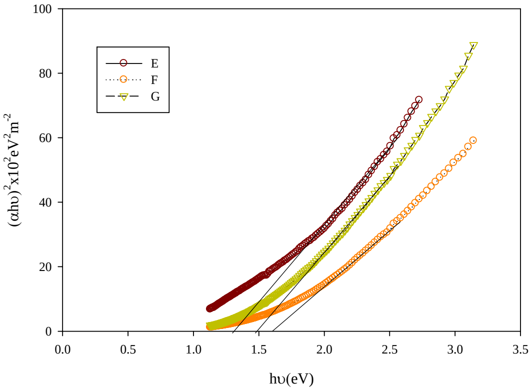

Fig. 5. The graph of Density of States as a function of Photon energy for TiO_2 – PbO thin films: Effects of varying concentration of $Pb(CH_3COO)_2$. $3H_2O$.

Compositional analysis: The elemental composition and chemical states of the samples were analyzed by Rutherford Backscattering (RBS) (see Fig. 6). It can be deduced that the stoichiometry of Oxygen (O): Titanium (Ti): Lead (Pb) is 0.758: 0.156: 0.086. The relatively low (trace) quantity of Pb in the film implies that Pb acts as an impurity element. The films deposited can thus be said to be $Ti_{0.156}O_{0.758}Pb_{0.086}$. The deposited film has thickness of 450 nm which is far lower than 520 nm of pure TiO_2. This no doubt will enhance the photocatalytic and hence the biocidal activity of the film. The advantage of this is that by reducing the size of the TiO_2 particle, the surface area of TiO_2 increases leading to improvement of photo – efficiency and thus photocatalytic property, because high surface area would make the surface of the particle more active to light and H_2O absorption. These observed trends of the properties of the films support the fact that they can be harnessed for possible application in collection of solar thermal radiation.

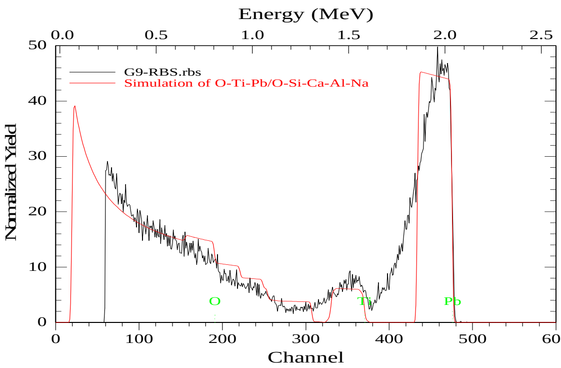

Fig. 6. The Rutherford Back – Scattering (RBS) of TiO_2 – PbO thin films.

4. Conclusion

We have successful deposited and characterized TiO_2 doped with PbO at varying concentrations of

$Pb(CH_3COO)_2.3H_2O$. Data from the density of states and the optoelectronic properties of the film reveal that there is significant band gap narrowing of the film towards the absorption edge of the visible light spectrum. The overall effect of the varying concentrations of $Pb(CH_3COO)_2.3H_2O$ can be seen generally to be minimal on the band gap as they are all well below 2.0 eV, and as such absorbs in the visible spectrum. On comparison, sample **E** which showed band gap value of 1.34 eV offers the best optimum visible window application since it is more comparable to the operating band of photocatalysis of water. From the optoelectronic properties of the studied material, it can thus, be concluded that TiO_2 doped with PbO is a possible material for photocatalytic application and can be tuned for use as window materials and radiation collectors within the visible region.

Acknowledgement

This work was partially funded by Ebonyi State, Federal Republic of Nigeria (Award No: EBSG/SSB/FSA/040/VOL. VIII/039). The authors are grateful to all the Staff of Physics department, Solid State Unit, University of Nigeria, Nsukka; Engineering Material Development Institute (EMDI), Akure, Ondo State; and Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife for their help in the cause of developing and characterization of the samples used in this work.

References

[1] Z. Wenguang, Q. Xiaofeng, I. Violeta, C. Xing-Qiu, P. Hui, W. Wei, M. D. Nada, R. Tijana, M. M. Harry, M. P. Parans, G. M. S., H. W. Hanno, G. Baohua, E. Gyula, Z. Zhenyu, Phys. Rev. Lett. **103**, 226401 (2009).
[2] L. Yong-Mu, J. Ju-Hyun, A. Jun-Hyung, J. Young-Sun, J. Kyung-Ok, H. Kyu-Seog, K. Byung-Hoon, J. Cer. Proc. Res. **6**(4), 302 (2005).
[3] T. Umebayashi, T. Yamaki, H. Itoh, K. A. Appl. Phys. Letts. **81**(3), (2002).
[4] C. Kutal, N. Serpone, Photosensitive Metal Organic Systems (1993): Mechanistic Principles and Applications. American Chemical Society, Washington D.C.
[5] R. W. Matthews, (1993): in Phtotocatalytic Purification and Treatment of Water and Air, Ollis, D. F., Al-Ekabi, H., Eds. Elsevier: Amsterdam.
[6] G. Schmid, M. Baumle, M. Greekens, I. Heim, C. Osemann, T. Sawatowski, Chem. Soc. Rev. **28**, 179 (1999).
[7] A. Fujishima, X. T. Zhang, D. A. Tryk, Surf. Sci. Rep. **63**, 515 (2008).
[8] S. B. Zhang, J. Phys. Condens. Matter **14**, R881(2002).
[9] B. Simone, A. Eros, B. Marco, G L. Phys. Rev. B, **66**, 045202 (2002).
[10] M. Ferroni, V. Guidi, G. Martinelli, E. Comini, G. Sberveglieri, D. Boscarino, G. Della Mea, J. Appl. Phys. **88**, 2 (2002).

---

*Corresponding author: panaceamee@yahoo.com