EFFECT OF THERMAL ANNEALING ON THE OPTICAL AND STRUCTURAL, PROPERTIES OF PbO THIN FILM

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This paper presents the results of the optical and structural characterization of chemical bath deposited lead oxide thin film, carried out within the pores of PVA and treated thermally under annealing temperature of 100º and 250ºC. The bath for the deposited PbO was composed of lead acetate, ammonia, and PVA solution. The deposition was maintained at a temperature of 70ºC for 8hrs. The films generally show high transmittance (70-85%) in the visible/near infrared regions of the solar spectrum and therefore a good material for warming applications in the home and in Agriculture. The band gap of the film is in the range of 2.6 - 2.8 eV. The result shows that thermal annealing influences both optical properties and band gap energy of nanocrystalline PbO thin films.

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1. Introduction

From the point of view of cost reduction of photovoltaic devices, thin film technology has been identified as a possible solution. The efficiency of the devices depends largely on the properties of the materials used and on the applied deposition techniques. Various techniques are available for the deposition of polycrystalline thin films of semi conducting materials such as sol gel [1], ionized cluster beam deposition [2-3], dc reactive magnetron sputtering [4], pulsed laser deposition [5], chemical bath deposition [6-11]. Many of these methods are expensive and require high vacuum and controlled formation condition [12]. Chemical bath deposition is least demanding and with its simplicity makes it very attractive. This technology is based on the controlled released of the metal ion. In the case of oxide films, the decomposition follows a two-step process, decomposition of the hydrous film and its pyrolitic decomposition into the anhydrous film [16].

The theory of film deposition follows from the fact that a soluble solid compound in water dissolves until it is saturated and contains positive and negative ions in contact with the undissolved solid compound. At saturation, the ionic product equals the solubility product. But at super saturation, ionic product exceeds the solubility product, precipitation of these ions occur and deposition takes place on the substrate. Spontaneous precipitation is eliminated using an appropriate complexing agent. In this work NH_3 was used as a complexing agent to slow down the reaction for gradual release of the ions.

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2. Experimental details

2.1 Deposition of lead oxide (PbO) thin films

PbO thin films have been successfully deposited on glass slide using chemical bath deposition (CBD) techniques at temperature of 70°C for 8hrs. The following constitutes the chemical bath system; lead acetate ($Pb(CH_3COO)_2$ as a source of Pb^{2+}, ammonia (NH_3) which served as the complexing agent in a PVA medium. The PVA solution was prepared by adding 450ml of distilled water to 0.9g of solid PVA heated for 1hr and allowed to cool. The set-up was composed of 10ml of 1M Pb acetate, 40ml of PVA solution and 6ml of ammonia put in that order into 50ml beaker. Prior to deposition, the glass slide were thoroughly cleaned which provides nucleation centre for growth or good adhesion and uniform deposition of the films. With the aid of synthetic foam the substrate was suspended vertically in the mixture and left for 8hrs at a temperature of 70°C. The coated substrate was removed, rinsed with distilled water and dried in the air. The colour of the film deposited was white, which is lead hydroxide $Pb(OH)_2$ [10]. The equation for the reaction process occurring in the bath is as follows:

$$2NH_3 + 2NH_4OH \longleftrightarrow 2NH_4OH$$
$$Pb(CH_3COO)_2 + 2NH_4OH \longleftrightarrow Pb(OH)_2 + 2(NH_4CHCOO)$$

The films were annealed at 100ºC (sample B) and 250ºC (sample C) for 1hr. Sample A was left unannealed and used as control to study the effect of high temperature annealing on the deposited films.

2.2 The characterization of PbO thin films

Optical properties of chemical bath deposited PVA capped PbO nanocrystalline thin films were measured by using UNICO–CO-2102pc spectrophotometer at normal incidence of light in the wavelength range of 200-700nm. Optical band gap of the sample were calculated from the absorption spectra. The structure of the film was studied with X-ray diffractometer

3. Result and discussion

3.1 XRD Studies

Figure 1 shows the plot of peak intensity against 2θ values for the as-grown and two annealed thin films of lead oxide deposited in this work. The figure shows increase in the height of the peak with annealing, which is an indication that better crystalline structure was achieved by annealing the films at elevated temperature. Hence better quantum confinement could be achieved with suitable thermal annealing of thin films.

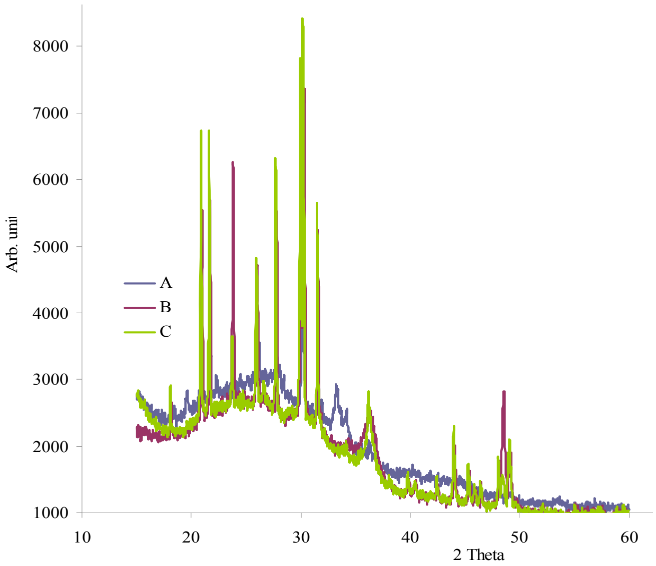

Fig 1. XRD pattern of lead oxide thin films.

3.2 Optical properties of PbO thin films

Fig 2 – 4, Show the variation of absorbance, transmittance and reflectance of the films with wavelength.

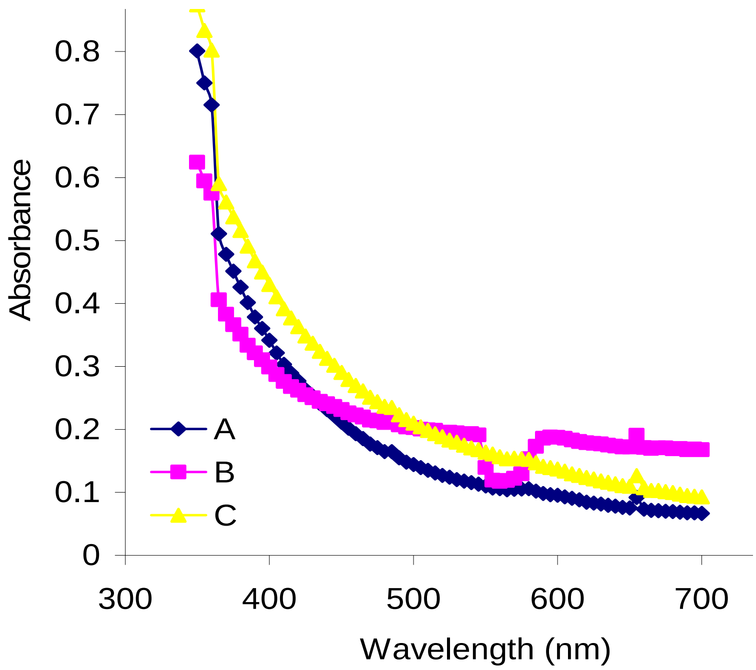

Fig. 2. Absorbance vs. wavelength for PbO thin films

The optical absorption spectra of the films deposited onto glass substrate were studied in the range of wavelength 200-700nm. Fig.2 shows that the film has highest absorbance of about 80% in the uv region. The absorbance increases with annealing temperature and the films annealed at 250^{o}C has the highest percentage of absorbance.

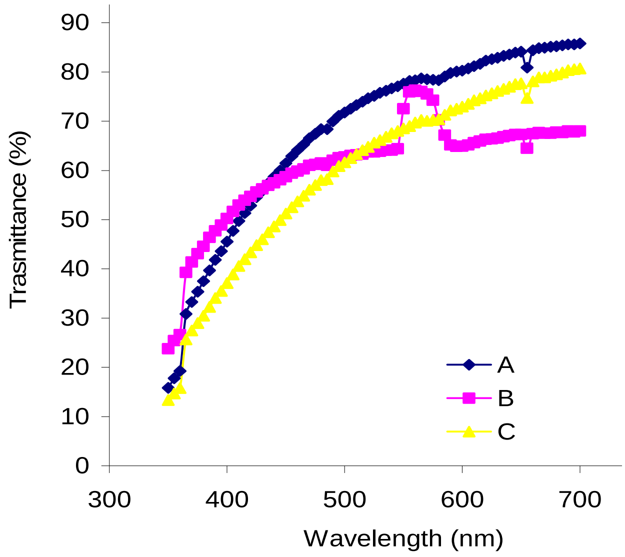

Fig. 3: Transmittance vs. wavelength for PbO thin films

A plot of transmittance against wavelength is shown in fig.3. The film has high transmittance in the visible spectrum. The highest percentage of transmittance (above 80%) corresponds to the as-grown film. A close observation of fig. 3 shows that thermal annealing reduced the optical transmittance of the PbO thin films deposited in this work. This may be as a result of increase in grain size and the decrease in the numbers of defects that is associated with high temperature annealing of thin films. [5, 16]. By filing the void in the film one expects denser films and hence a decrease in the transmittance of the films. Fig. 4 shows the spectral reflectance against wavelength for the samples under study. The figure shows a gradual decrease in the reflectance of the film with wavelength. The films exhibit on the average a reflectance of 15% within the visible region of the solar spectrum.

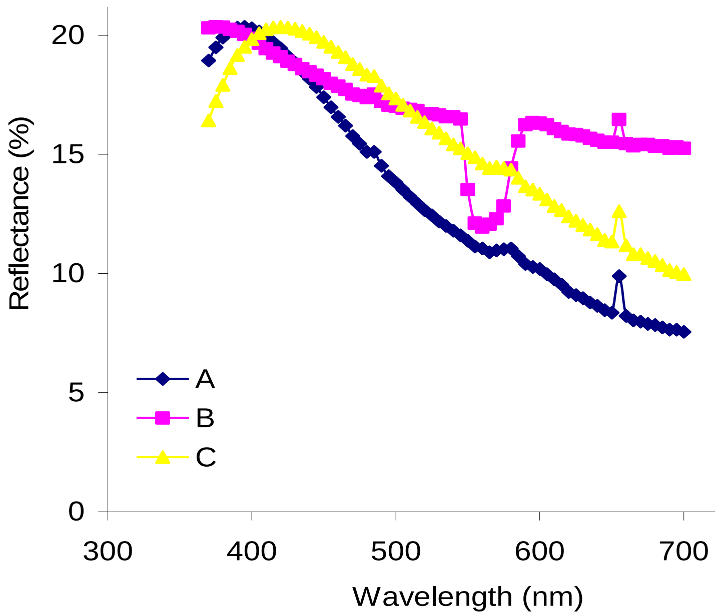

Fig.4: Reflectance vs. wavelength for PbO thin films.

Fig. 5 shows the relationship between the refractive index and the photon energy of the lead oxide film. The graph shows that the refractive index increases with photon energy to a maximum of 3.2eV.

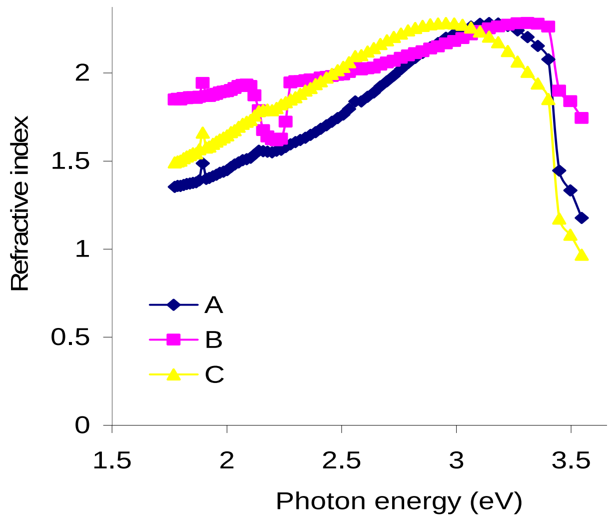

Fig. 5: Refractive index vs. photon energy for lead oxide thin films.

The thin films with high transmittance and low reflectance are good materials for antireflection coatings on transparent covers or window of solar thermal devices to reduce reflectance, increase transmittance and improve their efficiencies. The high transmittance and low reflectance properties of the as grown film are desirable characteristics for ideal solar control glazing to avoid glare problems and could be employed as thermal control coatings [16], It has been shown that thin films refractive index lower than 1.9 could be employed as anti-reflecting materials and could improve the transmittance of glass from 0.91 to 0.96 [18-19].

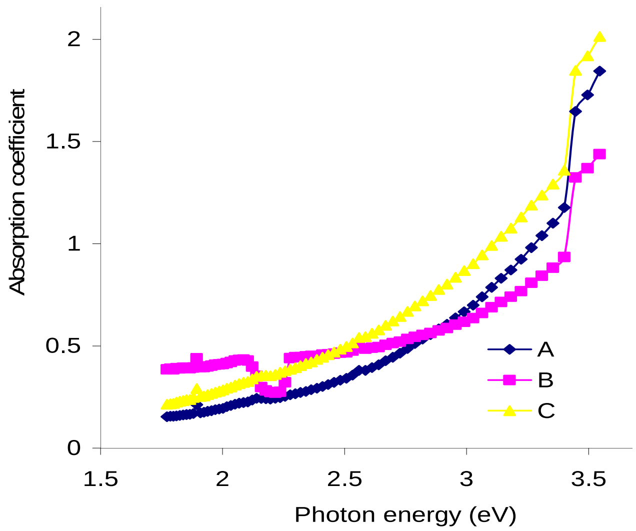

Fig 6: Absorption coefficient vs. photon energy for lead oxide thin films.

Fig. 6 is the plot of absorption coefficient against the photon energy for lead oxide thin film under study. The absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semi conductors are employed in the determination of the energy gap, Eg. The energy band gap for the thin film deposited in this work was calculated using the relation [23]: $\alpha=A(hv-Eg)^n/hv$, where A is constant, hv is the photon energy and α is the absorption coefficient, while n depends on the nature of transition. For direct transitions n=½ or 2/3, while for direct ones n=2 or 3 depending on whether they are allowed or forbidden, respectively. The obtained band gap energy were in the range of 2.60 – 2.85eV. High temperature annealing led to a decrease in the band gap energy of the films.

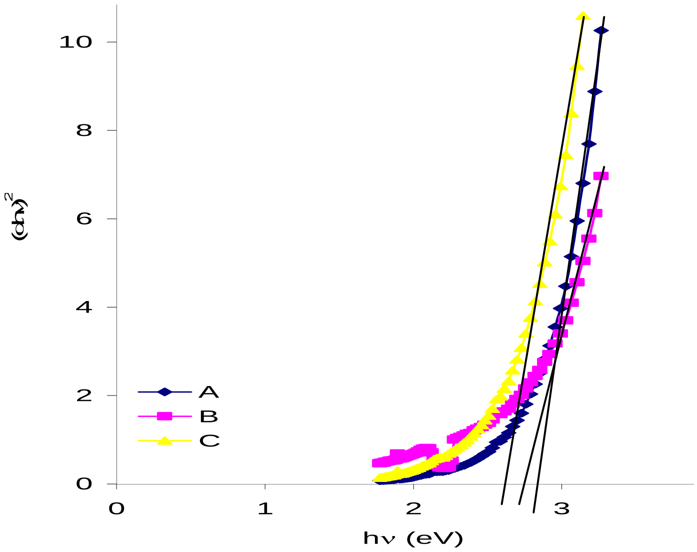

Fig.7: (ahv)² vs. hv for lead oxide thin films.

4. Conclusion

Lead oxide thin films have been successfully prepared by chemical bath deposition technique and annealed at different temperatures. XRD study reveals that high temperature annealing leads to better crystallization of the films. Optical studies and band gap analyzes show also that high temperature annealing has significant effect on the film properties.

References

[1] B. Dinghua, G. Haoshuang and K. Kuang, Thin Solid Films, **312**, 37 (1998).
[2] Sang Woo Whangbo, Hongkyu Jan, SanGon Kin, ManHo Cho, Kwngbo Jeong and Chung Nan, Whang; Journal of the Korean Physical society, **37**, 456 (2000).
[3] X. W. Sun, H. S. Kwok, Journal of Appl. Phys. **86**, 408 (1999).
[4] T. K. Subramanyan, B.S.A. Naidu and S. Uthanna, Crest. Res. Tech. **35**, 1193 (2000).
[5] J. S. Kim Howtz, A. Pique, C.H. Gilmore and D.B. Christy, Applied Physics A **69**, S447 (1999).
[6] F.I. Ezema, Greenwich Journal of Science and Technology, **32**, 1 (2003)
[7] A. Tanusevski, Science and Technology, **18**, 501 (2003).
[8] F.C. Eze and C.E. Okeke, Material Chemistry and Physics **47**, 31 (1997).
[9] M.T.S Nair and P.K. Nair Semiconductor Sci. Technology. **6**, 13 (1991)
[10] I.C. Ndukwe, Nig, Journal of Physic.**10**, 7 (1998)
[11] F.I. Ezema, and C.E. Okeke, Greenwich J.ScI. and Tech. **3**(2), 19 (2003).
[12] P.A. Pushparajoy, K. Arot, and S.J. Radhakrisne, Physics. D: Appl. Physics.27
[13] S yamage, A yoshikawa and H kasa, Japan J.Appl.Phys **26**, 1002 (1987)
[14] L Boone, S.A Howard and D.D Matin, Thin Solid films **176**,143 (1989)
[15] N.I Fainer, M. Kosinova Yu & M Rumyanetsov, Thin solid films **280**, 16 (1996)
[16] D.D.O Eya, A. J Ekponobi and C.E Okeke, Academic Open Internet Journal **14**, 2005.
[17] P.K Ghosh, S Jana,U.N. Maity and K.K. Chaltopadhyay, Physica E. 35(2006)
[18] S. C. Ezugwu, P. U. Asogwa, F. I Ezema, P. M. Ejikeme, J. Optoelectron. Adv. Mater. **8** 1765 (2010).
[19] S. A. Cetin and I. Hikmet; American Institute of Physics 978-7354 (2007).