Variation of optical and solid state properties with post deposition annealing in PVA-Capped MnO$_2$ thin films

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MnO$_2$ thin films were synthesized on glass substrate by chemical bath deposition technique within the pores of polyvinyl alcohol (PVA) at room temperature. The chemical bath for the deposition of MnO$_2$ is made up of solution of MnCl$_4$, NH$_4$Cl, NH$_3$, and PVA solution. The deposited films were annealed in air at 473K and 673K and characterized for the structural, morphological and optical properties. These properties were studied by means of X-ray diffraction (XRD), optical microscopy and optical spectrophotometer for their potential application in solar energy devices. From the absorption spectra, the calculated direct and indirect band gap energies lie respectively in the range of 1.8 – 2.5 eV and 0.8 and 1.2 eV. The films show good transmittance in the near infrared region of the solar spectrum. Post deposition annealing affects both the optical and solid state properties of the films.

Keywords: Chemical bulk deposition; Transparent semiconductor; Oxides thin films

1. Introduction

Thin film technology occupy a prominent place in basic research and the use of thin film semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs. The review of literature shows that thin film technology has been explored by many research groups. This has led to the emergence of several deposition techniques, most of which require steady/uninterrupted power supply because they involve high temperature process [1-4].

Nowadays, inorganic thin films with controlled morphology and properties can be fabricated using chemical bath deposition (CBD) technique [5 –7]. This technique is relatively simple, cost effective and suitable for deposition of films on large area substrate. Despite these advantages, only a few oxide thin films, notably ZnO and NiO, have gained wide popularity via this technique [8 –11].

In the last decade, synthesis and characterization of manganese oxides in various oxidation states and /or different structures have been intensified due to their promising potential for application in various fields, such as catalysis, secondary batteries and supercapacitors [12 – 16]. Out of these, only two reports were made in respect to the use of CBD technique [12, 13].

In the present study, we report the synthesis of binary manganese oxide of the type – MnO$_2$ in a PVA matrix via simple and inexpensive chemical bath deposition technique. The effect of post deposition annealing was studied by annealing the as-grown films in the oven at a temperature of between 473 and 673K.

2. Experimental

The chemical bath used for the preparation of the thin films in PVA matrix in this work was prepared in the following manner. First the PVA solution was prepared by adding 900 ml of distilled water to 1.8 g of solid PVA (-C$_2$H$_4$O)$_n$ (where n=1700), and stirred by a magnetic stirrer at 90 ^{o}C for 1hour. The solution was aged until the temperature drops to room temperature. To obtain deposition of MnO$_2$ thin films, the chemical bath was composed of 12 ml of 1M MnCl$_4$, 12 ml of 1M NH$_4$Cl, 12 ml of 10M NH$_4$OH and 40 ml of PVA solution put in that order into 80 ml beaker. A clean microslide was then inserted vertically through a synthetic foam into the mixture. The deposition was allowed to proceed at room temperature for 7 hrs after which the coated substrate was removed, washed well with distilled water and allowed to dry. Two of the deposited films were annealed in the oven at 473 and 673K, respectively, for one hour. One of the samples was left unannealed and used as control in order to study the effect of high temperature annealing on the deposited films.
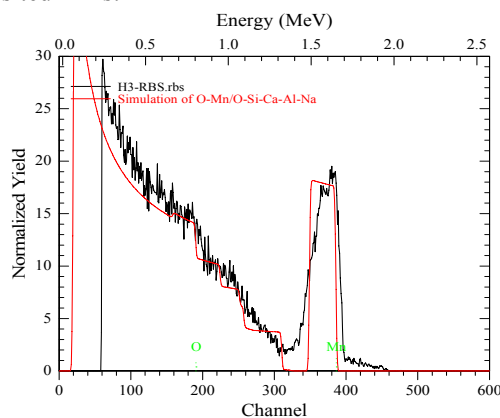

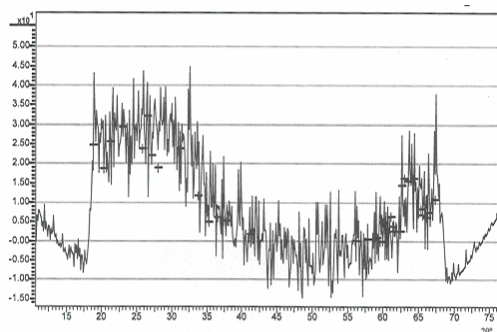**Figure 1.** RBS of MnO$_2$ thin film.

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Figure 2a. XRD pattern of the as-grown MnO$_2$ thin film.
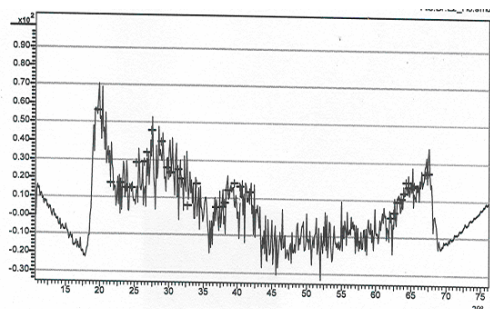

Figure 2b. XRD pattern of MnO$_2$ thin film annealed at 473K.
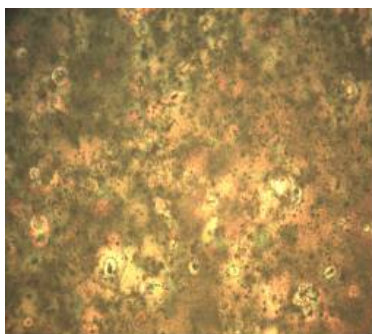

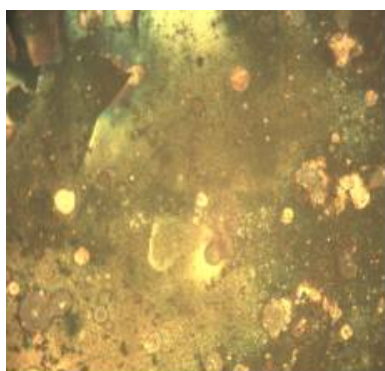**Figure 3a.** MnO$_2$ thin film (As-grown).

Figure 3b. MnO$_2$ thin film (annealed at 673K).

3. Characterization

The samples were characterized with XRD, RBS, and UV-VIS Spectrophotometer. Optical properties of chemical bath deposited PVA-capped MnO$_2$ thin films were measured at room temperature from Unico – UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000 nm. Optical band-gaps of the samples were calculated from the absorption spectra. X-ray diffraction (XRD) is an efficient tool for the structural analysis of crystalline materials. The XRD patterns for the samples were recorded using Philips PW 1500 X-ray diffractometer of CuKα wavelength (1.5408Å). The composition of the films was determined by using Rutherford back scattering.

4. Results and discussion

The elemental composition and chemical states of sample H$_3$ (film annealed in the oven at 473K) was analysed by Rutherford Backscattering (RSB) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The results are presented in Fig.1. From the film composition presented in table 1, we can deduce that the thin film of MnO$_2$ deposited has no impurity content. The RBS analysis also shows that the film has a thickness of 350 nm, and was deposited on 150000 nm thick glass substrate.

Figure 2 shows the XRD patterns of MnO$_2$ thin films deposited in this work. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films. A close examination of the two diffractograms shows an improvement in the crystallinity of the films when annealed. A comparison between the spectra of the two films in (a) and (b) show that there is more crystallization and more orientation of the crystal growth in the case of the film annealed at 473K. The lines became stronger with slight preferential orientation (2θ = 28.84°) that corresponds to (310) plane (JCPDS 44-0141). The surface microstructure of the films were obtained by taking photomicrographs of the films coated on the transparent glass slides with a wide KPL-W10x/18 Zeiss of the optical micrographs of MnO$_2$ thin films shows that the film annealed at 673K covers the substrate well, while the grains are well distributed throughout the surface.

Figure 4 and 5 give the absorbance and transmittance against the wavelength for MnO$_2$ thin films deposited in this work. A close observation of figure 4 shows that the film annealed at 673K has high absorbance in the visible portion of the solar spectrum, which decreases gradually as the wavelength increases. Both the as-grown film and the film annealed at 473K show poor absorption in the infrared spectrum. Figure 5 shows that high temperature annealing has significant effects on the transmittance of the films deposited in this work. While the as-grown film and the film annealed at 473K have high transmittance values in both the VIS and NIR portion of the solar spectrum, the highest temperature annealed film transmits poorly in this
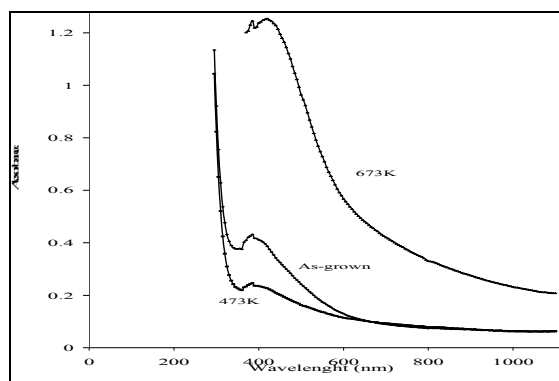
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Figure 4. Plot of absorbance against wavelength for MnO$_2$ thin films.
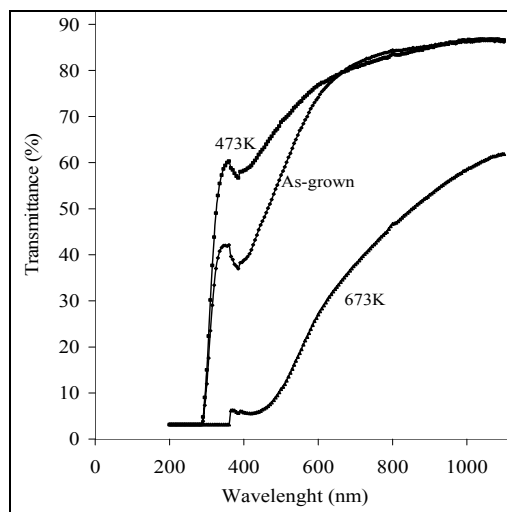

Figure 5. Plot of transmittance against wavelength for MnO$_2$ thin films.
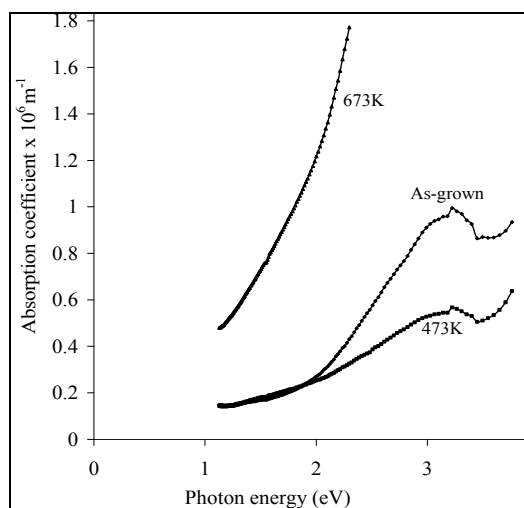

Figure 6. Plot of absorption coefficient against photon energy for MnO$_2$ thin films.
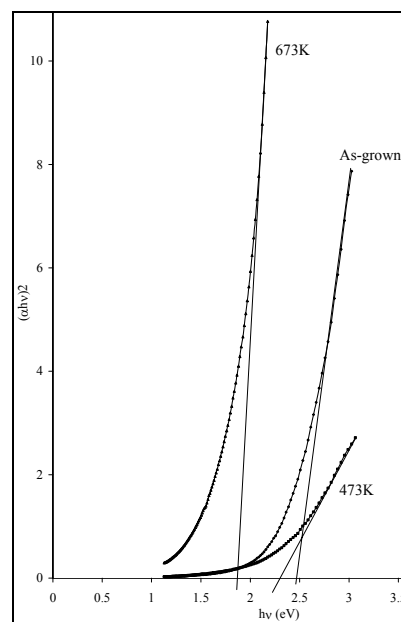

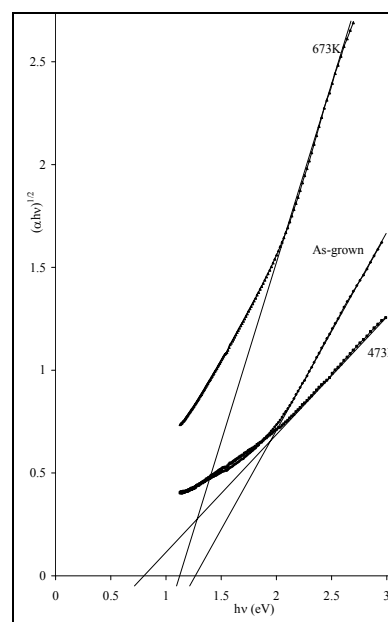**Figure 7.** Direct band gap plot.

Figure 8. Indirect band gap plot.

region. However, both figures show a slight lack of trend in the absorbance and transmittance values of the as-grown film and the film annealed at 473K within the visible portion of solar spectrum. The cause of this is not easily discernable. It could have resulted from unforeseen deposition conditions.

The details of the mathematical determination of the absorption coefficient (α) can be found in literature [17, 18]. The plots of absorption coefficient against photon energy are shown in figure 6.

These absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure

of semiconductors, are employed in the determination of the energy gap, E_g. The E_g was calculated using the well known Tauc's relation: $\alpha = A(h\nu - E_g)^n /h\nu$,

Where A is a constant, $h\nu$ is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions $n = \frac{1}{2}$ or $\frac{2}{3}$, while for indirect ones $n = 2$ or 3, depending on whether they are allowed or forbidden, respectively.

The best fit of the experimental curve to a band gap semiconductor absorption function was obtained for $n = \frac{1}{2}$ to obtain direct band gap energy values, and $n = 2$ for the indirect energy band gap values.

The calculated values of the direct energy band gap, from figure 7 lie in the range of 1.80 – 2.45eV. The values obtained for the indirect energy band gap lie within 0.80 –

1.30eV. Annealing the sample in oven lowers the values of both the direct and the indirect band gap energy of MnO_2 under study. This may be a consequence of the increase in crystallite size associated with high temperature annealing [21]. So the band gap decreases at higher annealing temperatures as a result of the increase in crystallite size based on the effective mass approximation: [22]

$$\Delta E_g = \hbar^2\pi^2/2R^2\{1/m_e + 1/m_h\} - (1.786e^2)/\jmath R$$

Where m_e, m_h are the effective masses of electrons in the conduction band and of holes in the valence band, respectively, and $\jmath$ is the static dielectric constant of the material. ΔE_g is the increase in band gap of the semiconducting material. The first term in the above equation represents the particle-in-a-box quantum localization energy and has simple $1/R^2$ dependence, where R is the particle radius; the second term represents the Coulomb energy with $1/R$ dependence. Hence, as R increases due to the increase in the crystallite size associated with high temperature annealing, the value of ΔE_g will decrease. Literature survey show: (1) that processes that increase the particle size decreases the band gap of most thin films [21, 23-24], (2) that a decrease in the energy band gap occurs in most cases with post deposition annealing [25-27]. The direct band gap energy for the as-grown film obtained here compare well with the value 2.54eV reported in literature for a different stiochiometry of manganese oxide [12]. However, the obtained band gap values in this work are much higher than the value (0.28eV) reported for spray-deposited MnO_2 thin films [28]. The high value may be attributed to better quantum confinement effect of MnO_2 crystals reported here. The data presented in figures 7 and 8 show that MnO_2 thin films can undergo both direct and indirect transitions. However, the gap between the valence and conduction band for the indirect transition is small compared to that of direct transition.

5. Conclusion

MnO_2 thin films have been successfully deposited onto glass slide using chemical bath deposition technique. XRD study reveals better crystallization of the films at higher annealing temperature. Optical studies and band gap analysis show that high temperature annealing has significant effect on these properties. The films have high transmittance in the VIS and NIR regions of the solar spectrum. The film can undergo both direct and indirect transition from valence to conduction band.

Reference

[1] L.W.Guo, D.L. Peng, H. Makino, K. Inaba, H.J. Ko, K. Sumiyama and T. Yao, J. Magn. Mater. **213**, 321(2000).
[2] X.H. Xu, X.F. Qin, F. X. Jiang, X. L. Li, Y. Chen and G.A. Gehring, Appl. Surf. Sci., **258**, 4956(2008).
[3] P.M. Rorvik, A. Almli, A.T.J. Helvoort, R. Holmestad, T. Tybell, T. Grande and M.A. Einarsrud, Nanotechnology **19**, 225605(2008).
[4] M.A. Flores-Gonzalez, M. Villanueva-Ibanez and J.L. Diaz de Leon Santiago, Superficies y Vacio **19**, 23 (2006).
[5] [F.I. Ezema, P.U. Asogwa, A.B.C. Ekwealor, P.E. Ugwuoke and R.U. Osuji, J. of the University of Chem Tech and Matall. 42, 217(2007).
[6] S.C Ezugwu, F.I Ezema, R.U. Osuji, P.U. Asogwa, B.A. Ezekoye, A.B.C. Ekwealor, C.Chigbo, M. Anusuya, M. Mahaboob Beevi, Optoelectronics and Advanced Materials – Rapid Communications **3**, 528(2009).
[7] P. U. Asogwa, S. C. Ezugwu, F.I. Ezema, A.B.C. Ekwealor, B.A. Ezekoye, R.U. Osuji, J. Optoelectronics and Advanced Materials. **11**, 940 (2009)
[8] V.R. Shinde C.D. Lokhande R.S. Mane and S.H. Han, Appl. Surf. Sci **245**, 407(2005).
[9] M.A. Vaidales-Hurtado, A. Mendoza-Galan, Mat. Chem and Phy. **107**, 33(2008).
[10] X.H. Xia, J.P. Tu, J. Zhang, X.L. Wang, H. Huang, Sloar Energy Mat & Solar Cells **92**, 628(2008).
[11] M.A. Vidales-Hurtado, A. Mendoza-Galvan, Sold State Ion.(2008), dio:10:1016/j.ssi.2008.07.003
[12] H.Y. Xu, S.L. Xu, X.D. Li, H. Wang and H. Yan, Appl. Surf. Sci **252**, 4091(2006).
[13] H. Unama, T. Kanehama, K. Yamamoto, K. Watanabe, T. Ogata and M. Sugawara, J. Mater. Sci. **38**, 255(2003).
[14] C.L. Shao, H.Y. Guan, S.B. Wen and B.Chen, Chinese Chem. Lett. **15**, 471(2004).
[15] Y.T. Wu and C.C. Hu, Electroch and Solid-State Lett. **8**(5), A240 (2005).
[16] X. Huang, D. Lv, H. Yue, Attia and Y. Yang, Nanotechnology **19**, 225606 (2008).
[17] W. Lou, X. Wang, M. Chen and J. Hao, Nanotechnology **19**, 225607(2008).
[18] J.P. Cheng, X.B. Zhang, Z.Q. Luo, Surf. and Coatings Tech. **202**, 4681(2008).
[19] D.S. Dhawale, A.M. More, S.S. Latthe, K.Y. Rajpure, C.D. Lokhande, App. Surf. Sci. **254**, 3269(2008).
[20] R.S. Vaidyanathan, INTERFACE **16**, 2(2007).
[21] S. Erat and H. Metin, Sixth International Conference of the Balkan Physical Union, 249 (2007).
[22] A. Popa, M. Lisca, V. Stancu, M. Buda, E. Pentia, T. Botila, J. Optoelectro. Adv. Mater. **8**(1), 43 (2006).

[23] A. Djelloul, K. Bouzid, F. Guerrab, Turk J. Phys. **32**, 1(2008).

[24] S. Jana, R. Thapa, R. Maity and K.K. Chattopadhyay, Physica E (2008), doi:10.1016/j.physe.2008.04.015.

[25] D. Soubane, A. Ihlal and G. Nouet, M.J. Condensed Matter, **9**, 32 (2007).

[26] F.I. Ezema, S.C. Ezugwu, R.U. Osuji, P.U. Asogwa, B.A. Ezekoye, A.B.C. Ekwealor and M.P. Ogbu, J. of Non-Oxide Glasses, **1**, 45 (2010).

[27] S.G. Kandalkar, C.D. Lokhande, R.S. Mane, S.H. Han, Appl. Surf. Sci. **253**, 3952 (2007).

[28] A.K.M. Farid Ul Islam, R. Islam and K.A. Khan, Renewable Energy, **30**, 2289 (2005).