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INFLUENCE OF PRECURSOR CONCENTRATION ON OPTICAL PROPERTIES OF Mn_xO_y THIN FILMS

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Precursor concentration dependent manganese oxide (Mn_xO_y) nanocrystalline thin films prepared by CBD techniques within the pores of PVP on glass slides at 343K were studied. The films turned out to be MnO_2 nanocrystals with grain size range of 76.11nm – 12.96nm for increasing precursor concentration. The deposited films were annealed at 403K and characterized for structural and optical properties. XRD analyses revealed their crystalline nature. The absorbance, transmittance reflectance, refractive index and absorption coefficient were found to vary inversely with precursor concentration, though irregularly. The absorption spectra showed that the energy band-gap of the films lies in the range of 2.34eV – 2.75eV.

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Keywords: Manganese oxide, precursor concentration, CBD, Structural and optical properties

1. Introduction

There are several thermodynamically stable manganese oxides such as Mn_3O_4, Mn_2O_3, and MnO_2 containing divalent, trivalent, and tetravalent manganese, respectively, in alkaline phase [1]. Manganese oxide films are relatively conductive, highly porous, and have high specific surface area [2]. Manganese oxides are distinguished by a rich variety of structural, electronic and magnetic properties that have rendered them materials of interest for numerous applications. The hydrated or amorphous manganese oxides have been paid much attention by many researchers recently [3–10] because of their low cost, great quantity and very high capability. Manganese oxide is also a promising pseudocapacitive electrode material for electrochemical capacitors because of its low cost, eco-friendly properties, and high theoretical specific capacitance [11–14].

Manganese oxide is used as electrode materials [15, 16], electrochemical capacitors [17, 18], rechargeable batteries, catalysts, sensors [19], magnetoelectronic devices [20] and supercapacitors [21].

There are many techniques to synthesize manganese oxides thin films such as sol-gel [20], thermal evaporation in vacuum [22], MOCVD [23], molecular beam epitaxy [24], atomic layer deposition [25] or Pulsed Laser Deposition (PLD) [26], chemical bath deposition (CBD) [27] etc. However not very much work had been done on manganese oxide with CBD technique. In this report, we present the influence of precursor concentration on the optical properties of manganese oxide.

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Synthesis of Manganese Oxide Mn_xO_y Films with Varying Precursor Concentration

The substrates were soaked in ethanol for 24 hours, washed with powder detergent solution, rinsed with doubly distilled water and dried in hot air, while the bath vessels were cleaned by washing thoroughly with solution of powder detergent. Five different baths, samples 11A – 11E, with varied concentrations of manganese salt were prepared as follows: Sample 11A was obtained by mixing 10ml of 0.1M $Mn(CH_3CO_2)_2$ (manganese acetate) salt with 4ml of NH_3 and 36ml of PVP in a 100 cm^3 beaker. Samples 11B, 11C, 11D and 11E were obtained as in sample 11A, but with the concentration of manganese acetate salt increased to 0.3M, 0.5M, 0.7M and 1.0M respectively. Substrates were then immersed in the baths of these samples and covered with synthetic foams. These were then kept in an oven at 343K for twelve hours to allow for substantial deposits. After twelve hours, they were removed, rinsed in distilled water and annealed at 403K in an oven for one and half hours.

Structural Characterization of Mn_xO_y Thin Films with Varying Precursor Concentration

The oxide films produced in this work were characterized by their surface morphology and preferred orientation. The surface microstructure of the films was obtained by taking photomicrographs of the films coated on the transparent glass slides with a wide KPL-W10x/18 Zeiss. For structural characterization, the films were subjected to X-ray diffraction (XRD), in the range of scanning angle 2θ with Cukα radiation (λ = 1.5406Å) using Philips P.W 1500 X-ray diffractometer.

2. Results and Discussion

Fig 1 gives the XRD spectrum for the as deposited Mn_xO_y film. The deposited film is Manganese Oxide, MnO_2. For this film, peak values were obtained at 2θ = 26.40º, 33.90º, 36.70º, and 62.70º corresponding to diffraction lines produced by different planes. Some of these peaks compare favourably with those obtained by Lai W.H et al [28].

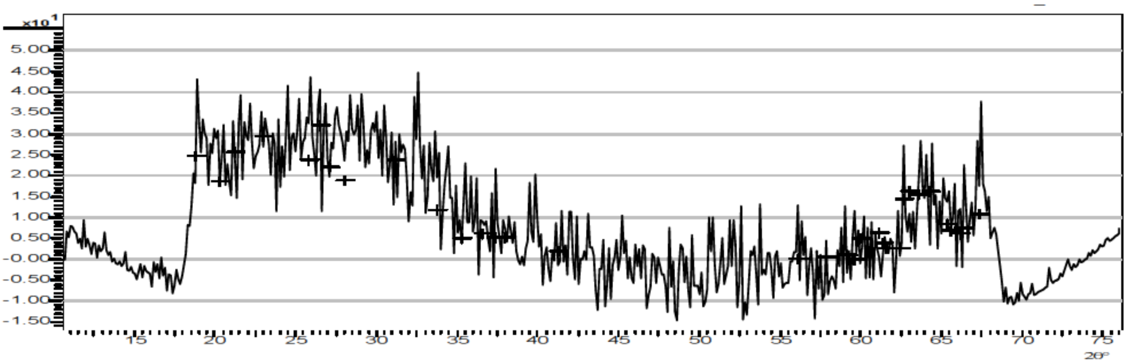

Fig 1: XRD diffractogram for as deposited MnO_2 films

Typical micrograph images are shown in Fig 2, for films with precursor concentrations of 0.1M, 0.5M and 1.0M respectively. The observed increase in compactness of grains with increase in concentration indicates an enhancement in crystallinity of films and reduction in crystal size. These were confirmed by the crystallite sizes obtained by calculation using the Scherer's formula.

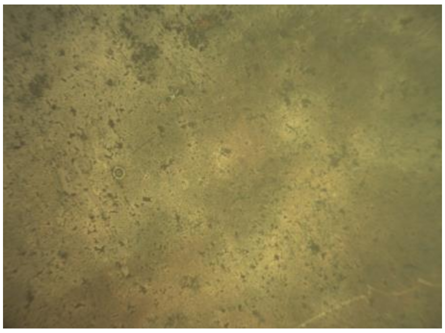

Fig 2(a): Manganese Oxide thin film with precursor concentration of 0.1M

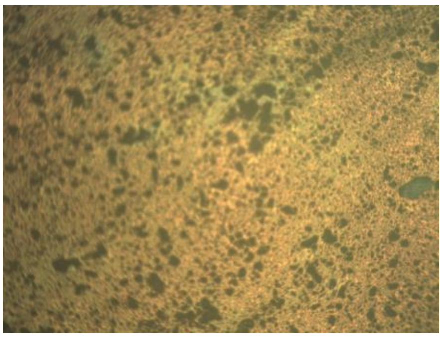

Fig 2(b): Manganese Oxide thin film with precursor concentration of 0.5M

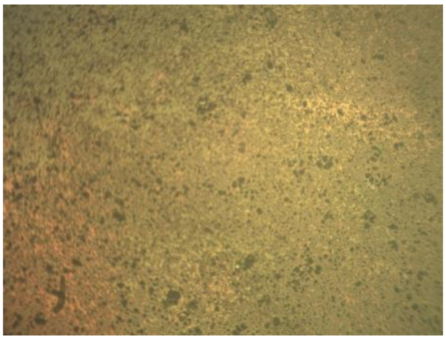

Fig 2(c): Manganese Oxide thin film with precursor concentration of 1.0M

Crystal Size

Using the Scherer's formula [29] $D = \frac{0.9\lambda}{\beta \cos\theta}$, where λ is wavelength of the x-ray, β is full width at half maximum (FWHM) of the peak with highest intensity and θ is the diffraction angle, the grain sizes were obtained to be in the range 76.11nm – 12.96nm for increasing precursor concentration. Thus the grain size of the films decreased with increase in precursor concentration though not consistently.

Optical Characterization of Mn_xO_y Thin Films with Varying Precursor Concentration

Using absorption spectra in UV–VIS–NIR regions obtained from Unico UV – 2102 PC spectrophotometer at normal incidence of light within the wavelength range 200nm – 1200nm, the optical properties of the films were studied.

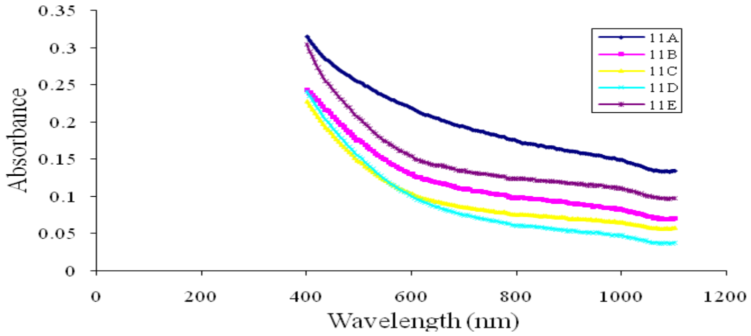

Fig 3: Absorbance spectra for MnO_2 thin films for varying precursor concentration

From fig 3 which is a plot of absorbance against wavelength, it can be observed that the absorbance of all the films with higher concentration (samples 11B – 11E) was low in the short wavelength region of the VIS, rapidly decreased to lower values in the long wavelength region of the VIS, and then gradually decreased to the NIR region. The film with the lowest concentration (sample 11A), however, showed higher absorbance than other films, which gradually decreased from the short wavelength region of the visible spectrum to the NIR region. The absorbance of the Mn_xO_y films showed a decrease, which may be attributed to increased film density, with increasing concentration of precursor.

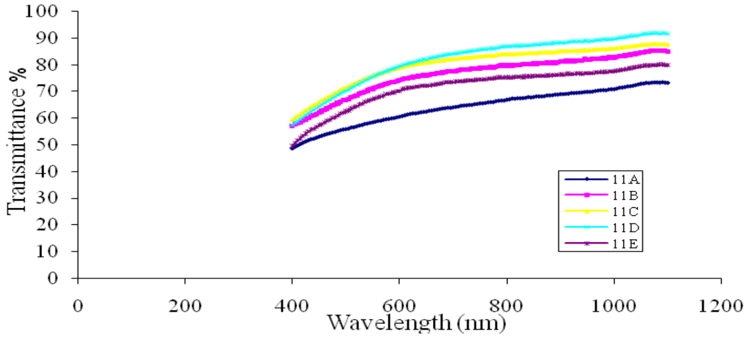

Fig 4: Transmittance spectra for MnO_2 thin films for varying precursor concentration

In fig 4 which gives the plot of transmittance against wavelength, the transmittance of all the samples was moderate, in the short wavelength region of the visible spectrum of radiation, but increased rapidly in the long wavelength region of the VIS to high values, and then gradually increased to the NIR region. The film with the lowest concentration (sample 11A) however had a lower transmittance than others. Transmittance on the other hand increased with increasing concentration of precursor. The high transmittance observed is in fair agreement with reports by Asogwa et al [27] and Thirumalairajan et al [29]. This high transmittance of the films in the long wavelength region of the visible spectrum can be employed to serve as coating for energy-saving or heat-protecting windows; while the high transmittance in the NIR suggests that it can be used as solar collectors in batteries [30], ion exchanger, [31, 32] and in catalysis [33].

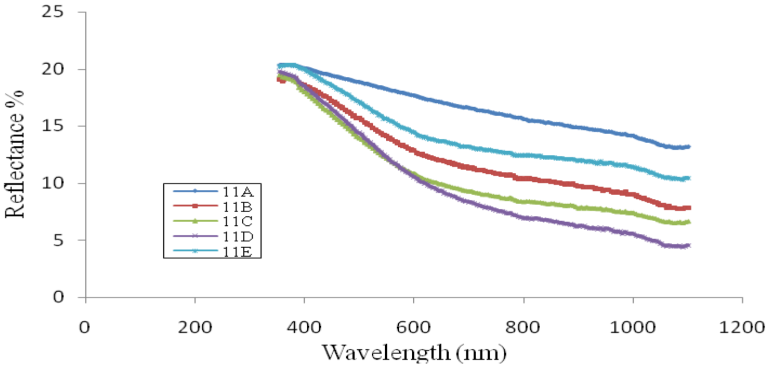

Fig 5: Reflectance spectra for MnO_2 thin films for varying precursor concentration

Fig 5 reveals that the reflectance of all the films (samples 11A – 11E) was low in the short wavelength region of VIS, but decreased rapidly for the films with higher concentration (samples 11B – 11E) in the long wavelength region of VIS and then gradually decreased to the NIR region. The film with the lowest concentration (sample 11A) however, had the highest reflectance in the short wavelength region of VIS, which decreased fairly linearly to the NIR region. The reflectance also showed a decrease as the concentration of precursor increased.

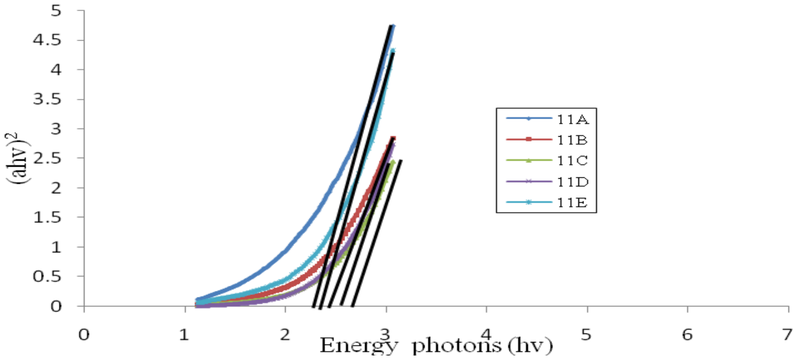

Fig 6: Band gap spectra for MnO_2 thin films for varying precursor concentration

From fig 6 it can be seen that the band-gap of the films of Mn_xO_y ranged from about 2.34eV – 2.75eV, with the band-gap of 11A being the least, followed by 11E, 11B**,** 11D and 11C respectively. These values agree with result obtained by Thirumalairajan, S et al [29], Xu, H.Y. et al. [34] and fairly with those obtained by Asogwa P.U [35]. The band-gap however, showed some irregular changes with increasing precursor concentration. The moderate band gaps of these films make them suitable for application as window layers in solar cell fabrication.

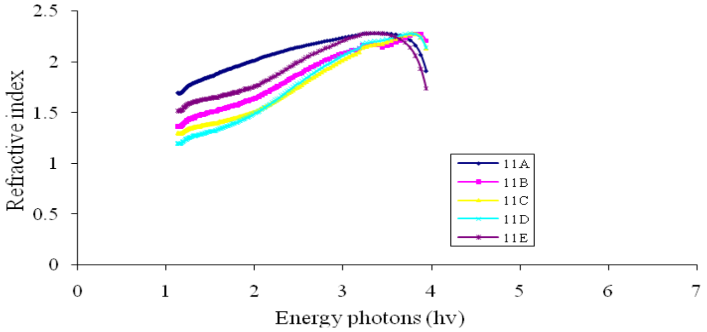

Fig 7: Refractive index spectra for MnO_2 thin films for varying precursor concentration

The refractive index, from fig 7, increased with increase in photon energy, and ranged from 1.1 – 2.3 for energy range 1.0eV – 3.5eV. Its value however decreased with increase in precursor concentration, though not systematically.

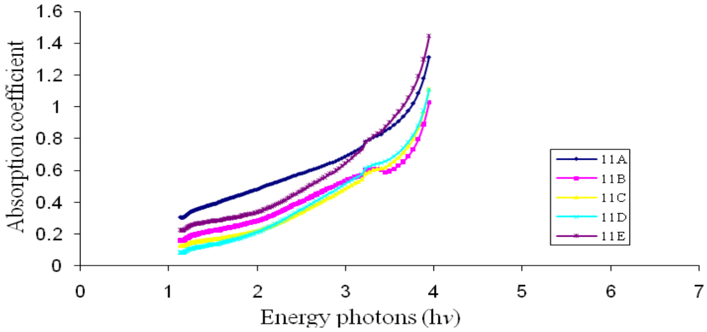

Fig 8: Absorption coefficient spectra for MnO_2 thin films for varying precursor concentration

The absorption coefficient increased gradually with increase in photon energy, and ranged from 0.08 – 0.35 for energy range 1.0eV – 3.5eV. It however did not have regular increase with increase in precursor concentration. This can be observed in fig 8.

3. Conclusion

Nanocrystal films of manganese oxide, MnO_2, have been successfully deposited on glass substrate by CBD techenique. The crystals obtained were of size range 12.96nm – 76.11nm. Some of the films have high transmittance in the long wavelength region of the visible spectrum which makes them suitable to serve as coating for energy-saving or heat-protecting windows; while the high transmittance of some in the near infrared region suggests that they can be used as solar collectors in batteries, ion exchanger and in catalysis. The energy band-gap of the films ranged from 2.34eV – 2.75eV. These moderate band-gap values make the films applicable as window layer in solar cell fabrication.

Reference

[1] M. Chiganez and M. Ishikawa, Journal of The Electrochemical Society, **147**(6), 2246 (2000).
[2] S. C. Pang and M. A. Anderson, J. Mater. Res., **15**(10), 2096 (2000).
[3] H. Y. Lee, J.B. Goodenough,“ Supercapacitor Behavior with KCl Electrolyte”, J. Solid State Chem., **144**, 220 (1999).
[4] J. Wei, N. Nagarajan, I. Zhitomirsky, J. Mater. Process. Technol., **186**, 356 (2007).
[5] M. Wu, G. A. Snook, G. Z. Chen, D. J. Fray, Electrochem. Commun., **6**, 499 (2004).
[6] R. N. Reddy, R.G. Reddy, J. Power Source, **124**, 330 (2003).
[7] D. J. Jones, E. Wortham, J. Rozi′ere, F. Favier, J. L. Pascal, L. Monconduit, J. Phys. Chem. Solids, **65**, 235 (2004).
[8] S. C. Pang, M. A. Anderson, T. W. Chapman, J. Electrochem. Soc., **147**, 444 (2000).
[9] J. H. Jiang, A. Kucernak, Electrochim. Acta, **47**, 2381 (2002).
[10] R. K. Sharma, H.-S. Oh, Y.-G. Shul, H. Kim, J. Power Sources, **173**, 1024 (2007).
[11] S. Chen, J.W. Zhu, X.D. Wu, Q.F. Han, X. Wang, ACS Nano **4,** 2822 (2010).
[12] H. Xia, M.O. Lai, L. Lu, J. Power Sources **196**, 2398 (2011).
[13] D.P. Dubal, D.S. Dhawale, R.R. Salunkhe, C.D. Lokhande, J. Alloys Compd. **496,** 370 (2010).

[14] Y. Lei, B. Daffos, P.L. Tabern, P. Simon, F. Favier, Electrochim. Acta **55,** 7454 (2010).
[15] J. C. Z. Nardi, J. Electrochem. Soc. **132,** 1787 (1985).
[16] L. Sanchez, J. Faray, J.P.Pereira –Ramos, L. Hernan, J. Morales, L. Tirado, J. Mater. Chem. **6,** 37 (1996)
[17] R. N. Reddy, R.G. Reddy, J. Power Sourc. **132,** 315 (2004).
[18] R. N. Reddy, R. G. Reddy, Electrochemical capacitor and hybrid powder sources, in: Brodd RJ, et al., (Eds), the electrochemical society proceeding series, PV 2002-7 Pennington NJ, 197 (2002).
[19] C-N Xu, K. Miyazaki, T. Watanable, Sensors and Actuators B **46**, 87 (1998).
[20] K. J. Kim, Y. R. Park. J. Cryst. Growth **270,** 162 (2004).
[21] Yu Hu, Hongwei Zhu, Jun Wang, Zhenxing Chen, Journal of Alloys and Compounds **509,** 10234 (2011).
[22] A. A. Dakhel, Thin Solid films **496,** 353 (2006).
[23] G-O. Yu, I. E. Graboy, V. A. Amelichev, A. A. Bosak, A. R. Kaul, B. Giittler, V.L. Sretchnikov, H.W. Zandbergen,. Solid State Comm. **124,** 15 (2002).
[24] L.W. Guo, D.L. Peng, H.Makino, T. Hanada, S.K. Hong, K. Sumiyama, T. Yao, K. Inaba, J. Appl. Phys. **90**, 351 (2001).
[25] O. Nilsen, H. Fjellvag, A. Kjekshus, Thin Solid Films **444**, 44 (2003).
[26] W. Neubeck, L. Ranno, M.B. Hunt, C. Vettier, D. Givord, Appl. Surf. Sci.**138**, 195 (1999).
[27] P.U. Asogwa, S.C. Ezugwu, F.I. Ezema, Superficies y Vacío **23**(1), 18 (2010).
[28] W. H. Lai, Y. H. Su, L.G. Toeh and M.H. Hon, Journal of Photochemistry and Photobiology A: Chemistry **195**, 307 (2008),.
[29] S. Thirumalairajan, K. Girija, M. Sudha, P. Maadeswaran, J. Chandrasekaran, Optoelectron. Adv. Mater. – Rapid Commun. **2**(12), 779 (2008).
[30] X.K Huang, H.J. Yue, A. Ttia, Y. Yang. J.Electrochem. Soc. **154**, A 26 (2006).
[31] M. Tsuji, S. Komarneni, Y. Tamaura, M. Abe. Mater. ResBull, **27**, 741 (1992)..
[32] M.Y.Lia, J.M.lin, J.H.Wang, C.T.Yang, T.L.Chou, B.H.Mok, N.S.Chong, H.Y.Tang, Electrochem. Commun. 5, 312 (2003).
[33] L.Espinal, S.L.Suib, J.F.Rusling, J.Am.Chem. Soc., **126**, 7676 (2004).
[34] H.Y. Xu, S.L. Xu, X.D. Li, H. Wang, and H. Yan, Chemical Bath Deposition of Hausmannite Mn_3O_4 Thin film. Applied Surface Science **252,** 4091 (2006).
[35] P.U. Asogwa, Journal of Optoelectronics and Biomedical Materials **2(**3), 109 (2010).