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Structural, Optical Investigation of Manganese Oxide Thin Films by Spray Pyrolysis Technique

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Research Article

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ABSTRACT

Thin films of MnO_2 are well suited for Electrochromic Photo-Voltaic (ECPV) effect and superconducting phenomenon (such as solar cells) due to its electrical and optical properties. MnO_2 thin films were prepared on glass substrate using a simple and low-cost chemical spray pyrolysis technique at different substrate temperature. The MnO_2 films were characterized by X-ray diffraction (XRD), transmittance and ultraviolet-visible (UV-VIS) optical spectroscopy. The XRD pattern reveals that MnO_2 films possess a cubic structure. The transmittance activity of the sample was carried out by optical absorption studies. The indirect band gap of the material increases with increase in temperature. The dynamic of ion exchange was studied with CV, CA and CE. The maximum colouration efficiency observed is 17 cm^2/C.

INTRODUCTION

Manganese oxide (MnO_2) is a transition metal oxide. It has many opto-electronic applications. It is black in color and is used as electrode materials[1, 2], rechargeable batteries, catalysts, sensors [3], electrochemical capacitors [4,5], magnetoelectronic devices [6].MnO_2 of different structures are depositedusing several techniques such as sol-gel [6], thermalevaporation in vacuum [10], MOCVD [10]. The MnO_2 was used as a substrate in the synthesis of magnetic oxide perovskite compounds, which have a variety of electrical and magnetic properties like metal-insulator transistors and a colossal magneto resistance [7-9]. MnO_2 of different structures are deposited using several techniques such as sol-gel [6], MOCVD [10], thermal evaporation in vacuum [11], spray pyrolysis [12].Manganeseoxide of different structure (MnO, Mn_2O_3, MnO_2 andMn_3O_4) is usually prepared by varying calculationscondition of starting chemical precursor bulk or film. They can also be prepared each other by varying thetemperature and atmosphere (vacuum or air, oxygen, hydrogen etc.,) of the calcinations [11]. $MnO_2$is preparedin the form of thin films on glass substrate by chemicalspray pyrolysis technique and their structural, opticalproperties are discussed. (Fig.1.1)

Experimental procedure

MnO_2 thin films were grown on glass substrate using a typical spray pyrolysis technique. The spraying solution was prepared by dissolving appropriate quantity of precursorpowder (manganese acetate) in methanolat room temperature according to the equation,

$H_2C\text{-}COOH$			$H_2C\text{-}COOH$	
|	$Mn.4H_2O$ +	$CH_3OH \rightarrow$	|	$Mn.5H_2O$
$H_2C\text{-}COOH$			$H_2C\text{-}COOCH_3$	
(Manganese acetate)		(Methanol)	(Complex)	

This solution is then atomized by compressed air at the pressure of 1 kg/cm^2 on to the ultrasonically cleaned glass substrates. The sprayed droplets undergo solvent evaporation, solute condensation and thermal decomposition thereby resulting in the formation of manganese oxide thin film. The chemical reaction that takes place is given by the equation,

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$$\begin{matrix} H_2C\text{-}COOH \\ | \\ H_2C\text{-}COOH \end{matrix} \; Mn.5H_2O \xrightarrow[(200\text{-}300^{0}C)]{Air} \begin{matrix} H_2C\text{-}COOH \\ | \\ H_2C\text{-}COOCH_3 \end{matrix} + MnO_2 + 2H_2O + 2H_2 \uparrow$$

(Manganese acetate)

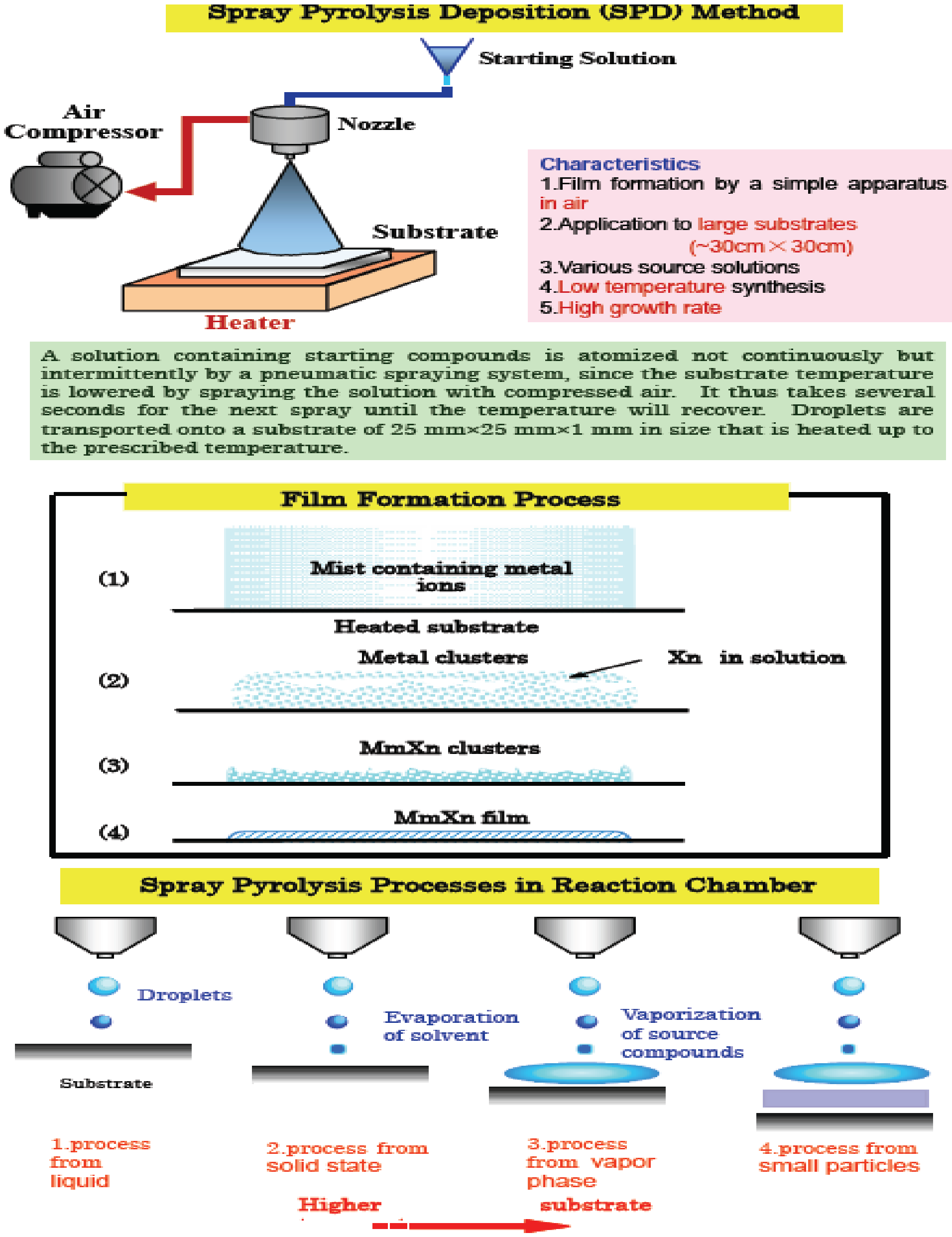

Fig.1.1 Spray pyrolysis technique

The substrate temperature was maintained at 200°C, 250 °C and 300 °C (± 2 °C) through a thermocouple as a sensor for temperature controller. The spray rate was kept constant at 12cc/min. The carrier gas flow rate was kept constant at 15 lit/min.

The MnO_2 films were subjected to X-ray diffraction technique to investigate the structural properties using anX-ray diffractometer (Philips PW1710) with CuKα radiation (λ = 1.5406 Å). Transmittances versus wavelengthmeasurements were made using UV-VIS- NIR spectrophotometer (Hitachi model 330).

RESULTS AND DISCUSSION

Structural analysis

The structural elucidation of MnO_2 film was shown in Fig. 1.2. The structural identification of MnO_2 thin films deposited at various substrate temperatures from manganese acetate was carried out with X-ray diffraction. (The diffraction pattern obtained for samples T1, T2, T3 are as shown in Fig. 1.2.) The observed XRD patterns were compared with the JCPDS data [12]. The observed'd' values agree well with the standard'd' values and it was observed that all samples exhibit peaks corresponding to (104), (001), (311), (400) planes. The existence of shift in some peaks is due to internal strain existing in the crystalline due to the disproportionate array of the constituents [13]. The comparison with JCPDS data confirms the formation of $Mn(OH)_2$ and MnO_2. The standard and observed'd' values with corresponding (hkl) planes are listed in Table 1.

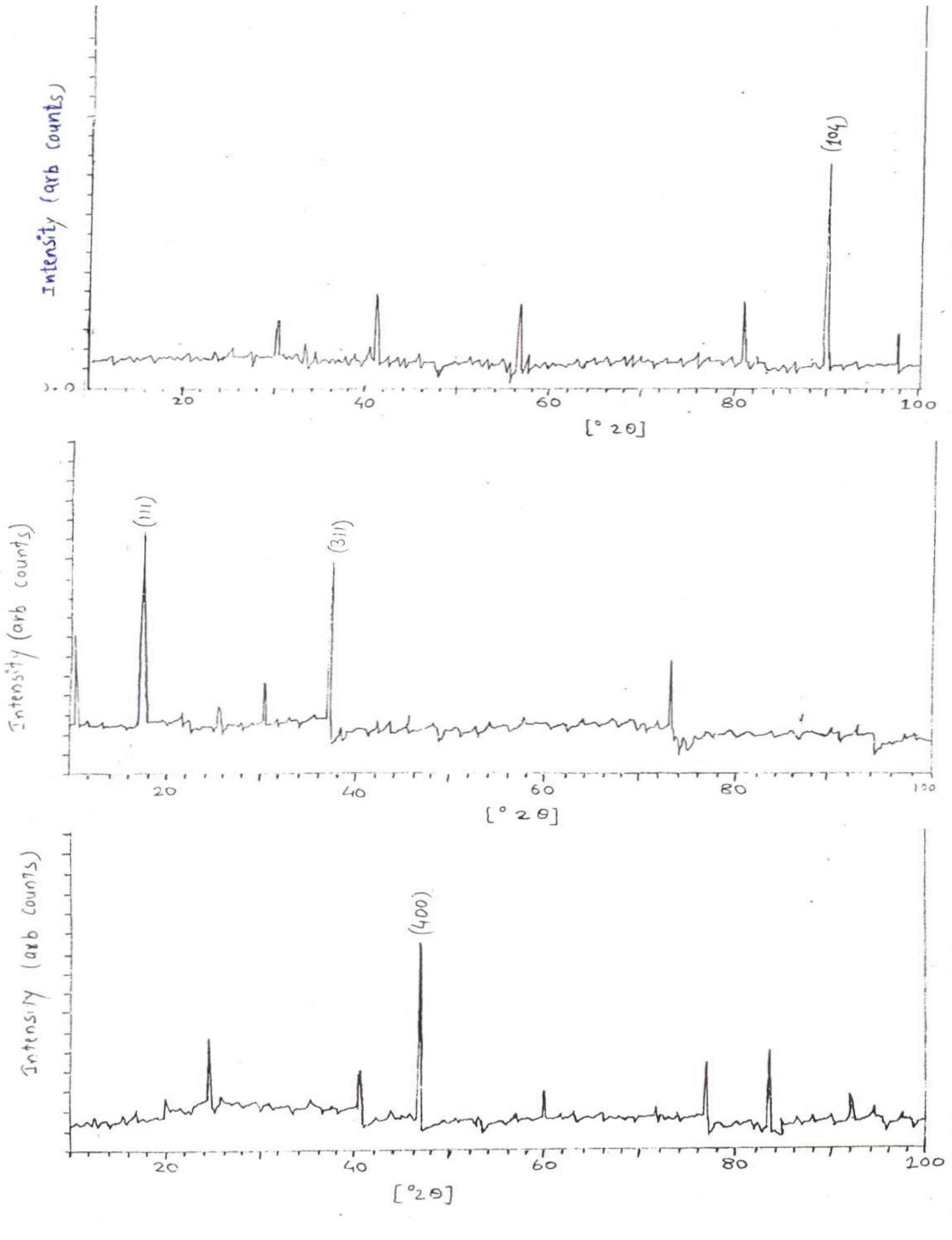

Fig.1.1 The diffraction pattern obtained for samples T1, T2, and T3

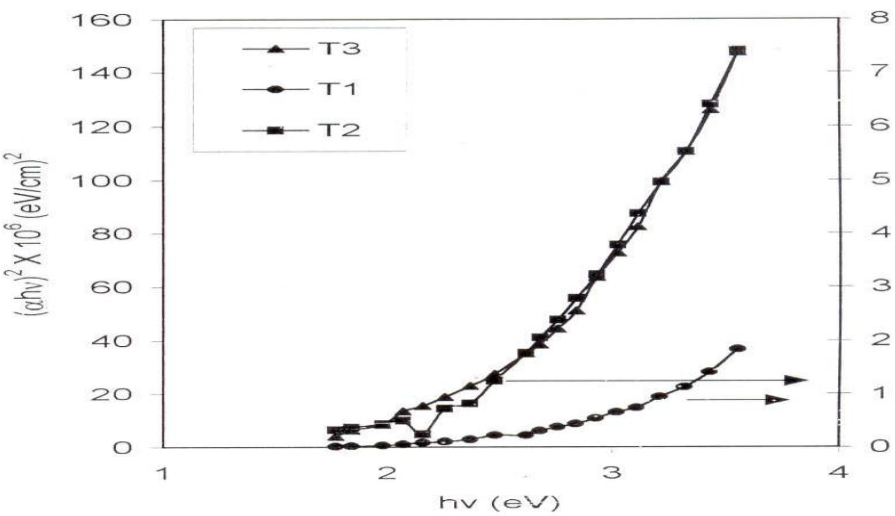

Fig.1.3. Direct band gap energy

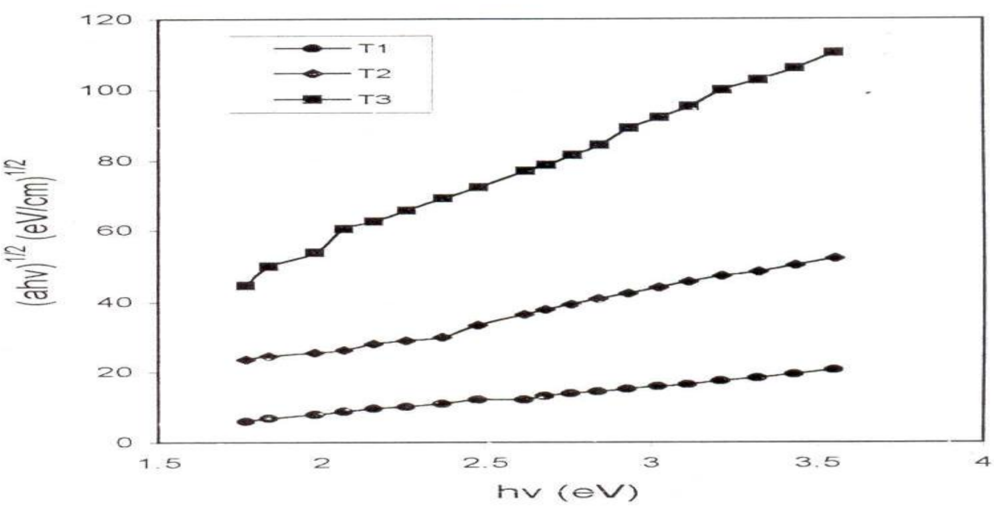

Fig.1.4. Indirect band gap energy

The samples T1 prepared at lower temperature 200°C consists of $Mn(OH)_2$ phase indicating an incomplete thermal decomposition of manganese acetate. It was also observed that the prominence of MnO_2 phase was found to improve with an increase in deposition temperature. The films prepared at 250°C consists of $Mn(OH)_2$& λ- MnO_2 and the films prepared at 300°C consists of λ- MnO_2 films.

Transmittance analysis

The films were further analyzed by optical absorption studies as well as transmittance study. The variation of optical absorption density 'αt' with the wavelength 'λ' for the films were carried in the wavelength range 400 to 800 nm with UV spectrometer. This optical data were further analyzed to calculate the band gap energy of MnO_2 samples using the relation,

$$\alpha = \alpha_o (h\nu - E_g)^n$$

Where α_o-constant, hν-photon energy, E_g - band gap energy

n= 1/2 for direct allowed transition
n = 2 for indirect allowed transition

Fig.1.3 shows the variation of $(\alpha h\nu)^2$ Vs (hν) for all samples and fig.1.4 shows the variation of $(\alpha h\nu)^{1/2}$ Vs (hν). The extrapolation of the straight line portions of the plots $(\alpha h\nu)^2$ Vs (hν) to zero absorption coefficient gives the values of direct band gap energy and extrapolation of the plots $(\alpha h\nu)^{1/2}$ Vs (hν) to gives the values of indirect band gap energy. It is found that indirect band gap of the samples increases with increase in temperature. The direct band gap energy for the samples at 250°C is minimum as compared to other samples.

Table 1: X-ray diffraction data table

Substrate temperature (°C)	observed'd' values (Å)	standard'd' values (Å)	(hkl)	Phase	System
200 (T1)	1.1041	1.0945	(104)	$Mn(OH)_2$	Hexagonal
250 (T2)	4.7362	4.734	(001)	$Mn(OH)_2$	Hexagonal
	2.4169	2.42	(311)	λ-MnO_2	Cubic
300 (T3)	1.9321	2.0100	(400)	λ-MnO_2	Cubic

CONCLUSIONS

MnO_2 thin films were prepared using by spray pyrolysis technique. The structural analysis revealed the cubical nature of the film; it is also observed that the prominence of MnO_2 phase was found to improve with an increase in deposition temperature. The indirect band gap energy of the material increases with increase in temperature.

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