

## EFFECT OF DEPOSITION MEDIUM ON THE OPTICAL AND SOLID STATE PROPERTIES OF ANNEALED MnO<sub>2</sub> THIN FILMS

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MnO<sub>2</sub> thin films were synthesized on the glass substrate by chemical bath deposition technique within the pores of polyvinyl alcohol (PVA) and polyvinyl pyrrolidone at room temperature. In order to study the effect of the capping polymer on the properties of these films, similar deposit was carried out using water as the deposition medium. A chemical synthesis process for the fabrication of MnO<sub>2</sub> thin films is presented herein. In this present work, these films were annealed in the oven at 200°C and 400°C and characterized for the structural, composition and optical properties. These properties were studied by means of X-ray diffraction (XRD), Rutherford backscattering (RBS) and optical spectrophotometer. The optical properties revealed the presence of direct band gaps with energies in the range of 1.40 – 2.05eV (for the films deposited in water medium), 1.60 – 2.30eV (films deposited in PVA medium) and 1.40 – 1.90eV (films deposited in PVP medium). The films show high transmittance in the visible and near infrared region of the solar spectrum.

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### 1. Introduction

The usefulness of the optical properties of Metal, Chalcogenide and Oxide films has been responsible for the immense interest in the study of science and technology of thin films. The technology and understanding of films less than 1 micron thick have made tremendous advances in the last decades, owing to the industrial demand for reliable thin film microelectronics devices to fulfil the need of the sputnik era. Thin films have mechanical, electrical, magnetic and optical properties, which in most cases, differ from those of the bulk material and are used commonly in the form of a deposit on a suitable substrate for integrated circuits, resistors, capacitors, transistors and superconductors.

In particular, MnO<sub>2</sub> thin films have been found useful in batteries [1,2], ion exchange [3,4], catalysis [5] and oxidation process [6,7]. The reported polymorphs of manganese dioxide (MnO<sub>2</sub>) includes  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -MnO<sub>2</sub> [8]. The performance of MnO<sub>2</sub> is influenced significantly by the crystal type, size and morphology [9]. Thin film deposition carried out within a polymer matrix is a suitable means of modifying the crystallite size [10].

The prevalent preparative method used for the deposition of MnO<sub>x</sub> thin films includes the sol-gel method [11-13] and anodic oxidation of Mn<sup>2+</sup> [14]. However, it has been reviewed and shown that direct deposition of oxide thin films from aqueous solutions has advantages over the above-mentioned techniques because it enables us to prepare oxide thin films on non-conducting, less refractory substrates. The principles of the direct deposition of oxide thin films from aqueous solutions are based on a gradual increase in supersaturation of metal ions by means of spontaneous hydrolysis of soluble precursors [15-17] so that heterogeneous nucleation of films becomes more predominant than homogeneous nucleation.

In this report, the result of chemical bath deposited MnO<sub>2</sub> thin films in distilled water, polyvinyl alcohol (PVA) solution and polyvinyl pyrrolidone (PVP) solution as the deposition media is presented. The deposited films were annealed in the oven at elevated temperatures, characterized

and analysed in order to find the effects of both the deposition medium and the annealing temperature on the deposited films.

## 2. Experimental procedure

The preparation of  $MnO_2$  thin films on glass slide was carried out using chemical bath deposition technique. Prior to the deposition of the films, the PVA and PVP solutions were prepared. PVA solution was prepared by adding 900 ml of distilled water to 1.8 g of solid PVA and stirred by a magnetic stirrer at  $90^\circ C$  for 1 hour. The solution was aged until the temperature drops to room temperature. Solution of PVP was prepared by mixing 4g of solid PVP with 400ml of distilled water. The mixture was stirred with magnetic stirrer without heating until the solute completely dissolves.

The reaction baths for the deposition of  $MnO_2$  thin films contain 12ml of 1M  $MnCl_4$ , 12ml of 1M  $NH_4Cl$ , 12ml of 10M  $NH_4OH$  and 40 ml of the solution put in that order into 80ml beaker. A clean microslide was then inserted vertically through synthetic foam into the mixture. Two films each were deposited using distilled water, PVA solution and PVP solution. In each case the deposition lasted for 7 hrs, after which the coated substrate was removed from the bath, washed well with distilled water and allowed to dry. The samples were annealed in the oven at  $200^\circ C$  and  $400^\circ C$  for 1 hr. and labelled H2O\_H2, PVA\_H2, PVP\_H2 (for the samples annealed at  $200^\circ C$ ) and H2O\_H4, PVA\_H4, PVP\_H4 (annealed at  $400^\circ C$ )

Samples of the films deposited in PVA medium was used for XRD and RBS analyses. However, the optical properties of all the films deposited were measured at room temperature from Unico-UV-2102 PC double beam spectrophotometer with uncoated glass as reference.

## 3. Results and discussion

The elemental composition and chemical states of sample H<sub>3</sub> (film deposited in PVA medium and annealed in the oven at  $200^\circ C$ ) was analysed by Rutherford Backscattering (RSB) at Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria. The results are shown in fig.1. From the film composition presented in table 1, we can deduce that thin film of  $MnO_2$  deposited in this work 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.

Table 1: The composition of substrate and  $MnO_2$  film from RBS analysis

	Oxygen	Manganese	Silicon	Calcium	Aluminium	Sodium
$MnO_2$ thin film	0.643	0.357	-	-	-	-
Glass substrate	0.500	-	0.120	0.100	0.100	0.180

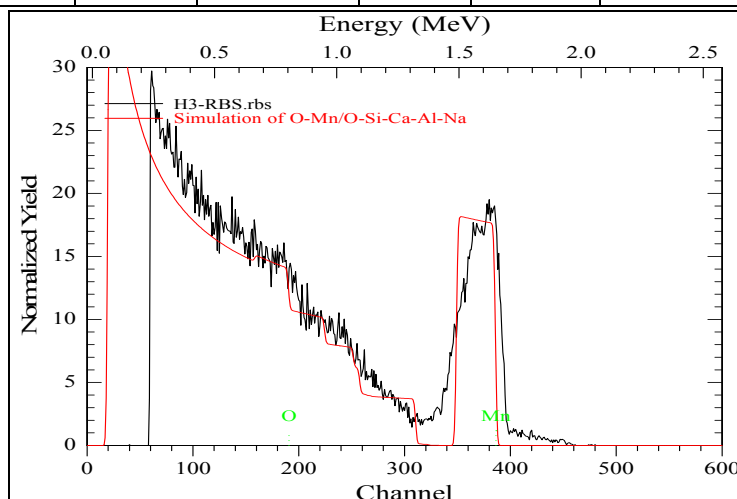


Fig.1. RBS of  $MnO_2$  thin film.

Fig. 2 shows the XRD patterns of MnO<sub>2</sub> thin films deposited in this work. Peak broadening has been observed in recorded diffraction patterns, which shows the formation of crystalline thin films. The reflection at a  $2\theta$  value of  $28.84^\circ$  corresponds to (310) plane of MnO<sub>2</sub> phase (JCPDS 44-0141).

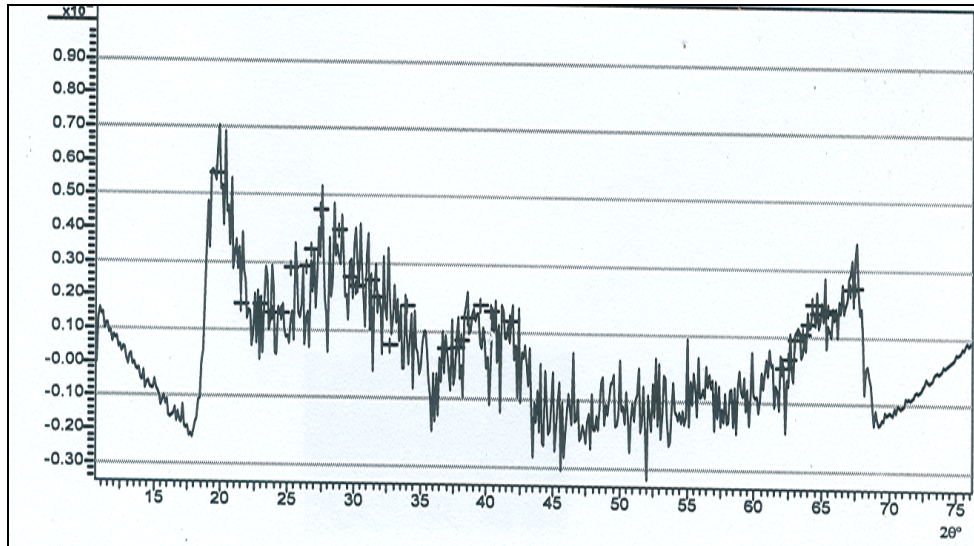


Fig. 2. XRD pattern of MnO<sub>2</sub> thin film annealed at 200°C

The UV-VIS-NIR absorption, transmission and reflection spectra of the MnO<sub>2</sub> films prepared in different media are shown in figs. 3 –5.

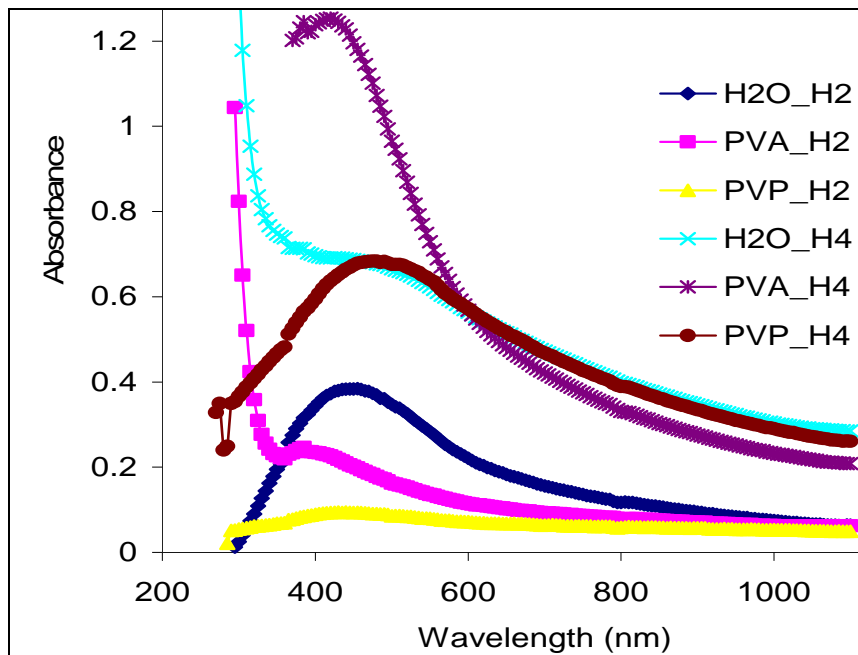


Fig.3. Absorption spectra of MnO<sub>2</sub> thin films deposited in different media

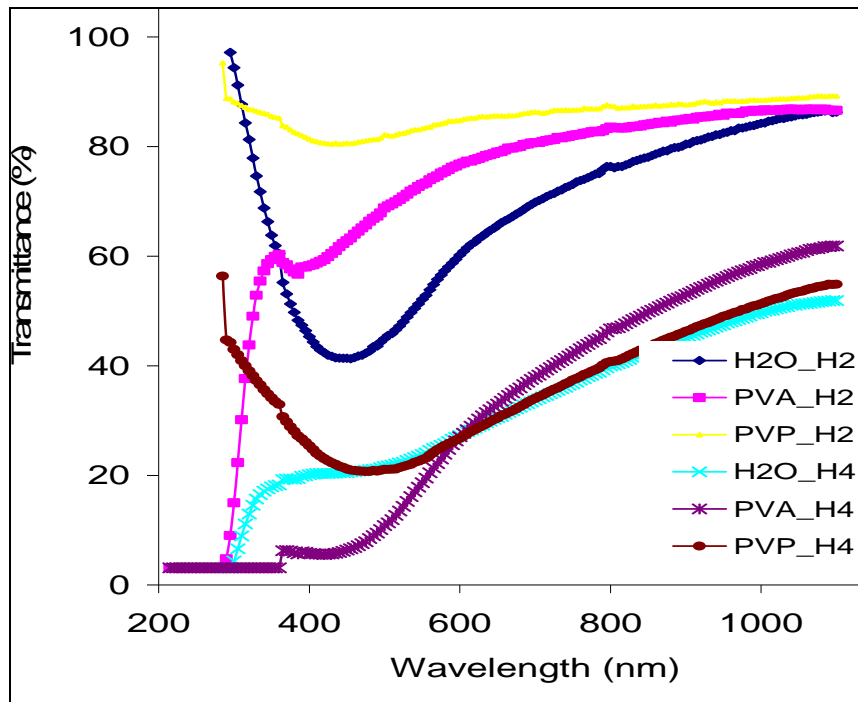


Fig.4. Transmission spectra of  $MnO_2$  thin films deposited in different media

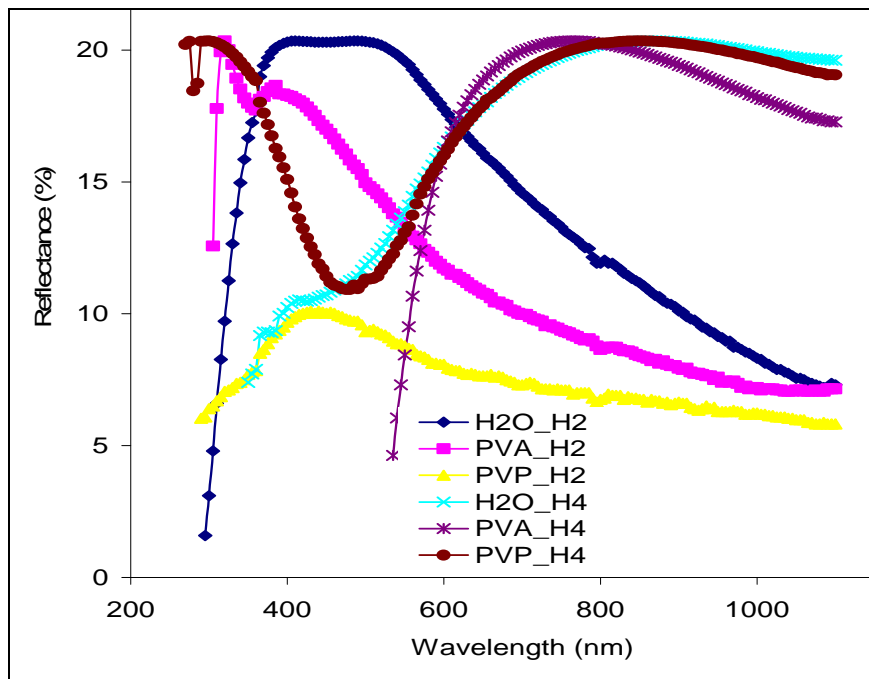


Fig.5. Reflection spectra of  $MnO_2$  thin films deposited in different media

Fig.3 shows that the films annealed in the oven at  $400^\circ\text{C}$  have higher absorption of visible portion of the solar light energy when compared with the films annealed at  $200^\circ\text{C}$ . Beyond  $400\text{nm}$ , the plot shows a gradual decrease in the absorbance of the films with wavelength. The highest increase in absorbance with annealing temperature is observed in the film deposited using PVP solution.

The films annealed at 200°C have high transparency in a wide wavelength range. The film deposited in PVP medium has the highest transparency in both the VIS and NIR region of the solar spectrum and is closely followed by the film deposited in PVA medium. A close observation of fig. 4 shows that the effect of annealing on the transmittance of MnO<sub>2</sub> thin films deposited in this work is more pronounced in the films deposited in PVP medium. Table 1 gives the average absorbance, transmittance and reflectance of the films deposited in different media and annealed at 200 and 400°C.

Table 1. Average absorbance, transmittance and reflectance of MnO<sub>2</sub> thin films within the wavelength range of 400 – 1100nm.

	H2O_H2	PVA_H2	PVP_H2	H2O_H4	PVA_H4	PVP_H4
Average Absorbance (%)	17.65	10.50	6.64	46.36	50.78	45.50
Average Transmittance (%)	68.49	79.00	85.86	36.15	38.10	36.99
Average Reflectance (%)	13.86	10.50	7.50	17.49	11.12	17.51

Fig. 6 is a plot of the absorption coefficient against photon energy for MnO<sub>2</sub> thin films deposited in different media and annealed at 200 and 400°C. Band to band transition in oxide films depends on the absorption coefficient  $\alpha$  and photon energy by the relation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)^{1/2} \quad (1)$$

Where A is constant,  $h\nu$  and  $E_g$  is the photon energy and optical band gap energy respectively. The value  $E_g$  is calculated by plotting  $(\alpha h\nu)^2$  vs.  $(h\nu)$  as in fig.7.

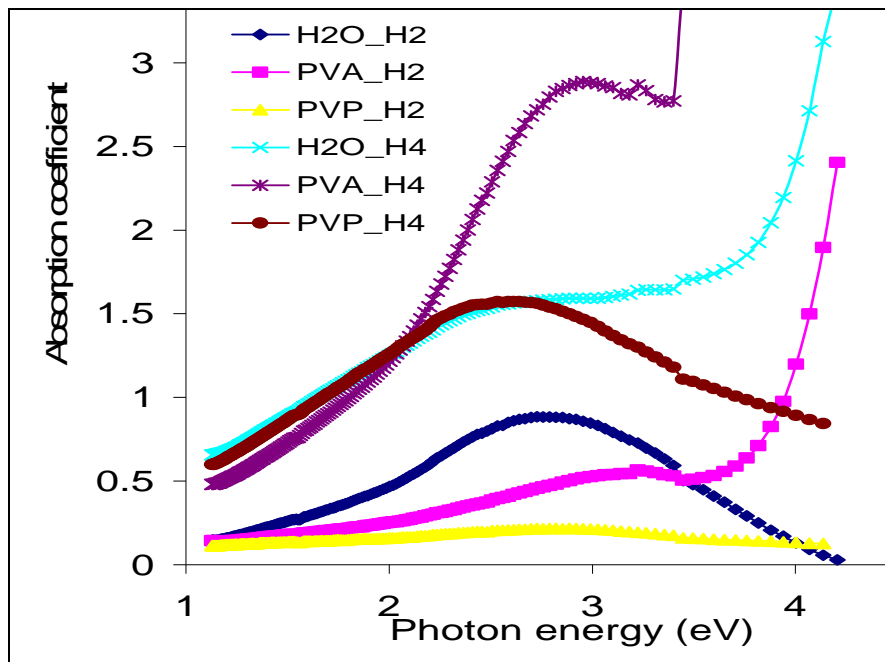


Fig.6. Plot of absorption coefficient vs. photon energy for MnO<sub>2</sub> thin films deposited in different media

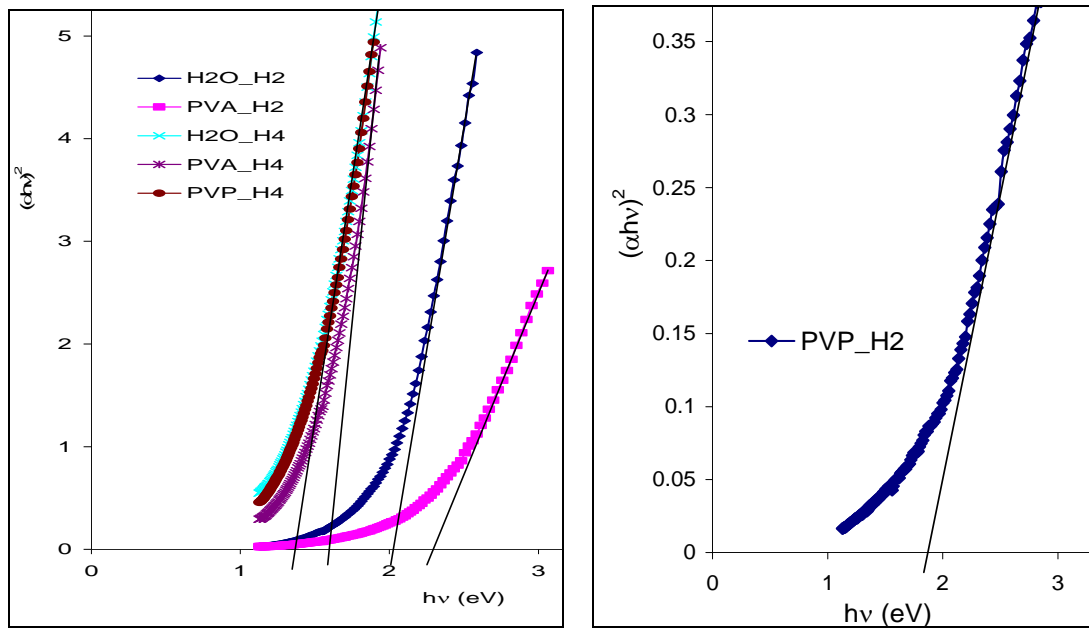


Fig.7. Plot of  $(\alpha hv)^2$  vs.  $(hv)$  for  $MnO_2$  thin films deposited in different media

It is observed from table 2 that high thermal annealing lowers the value of band gap energy of  $MnO_2$  thin films irrespective of the deposition medium. This may be a consequence of the increase in crystallite size associated with high temperature annealing [19]. So the band gap decreases at higher annealing temperatures as a result of the increase in crystallite size based on the effective mass approximation [20]. Literature survey shows that: (1) processes that increase the particle size decreases the band gap of most thin films [19, 21-22], (2) a decrease in the energy band gap occurs in most cases with post deposition annealing [18, 23-24]. The direct band gap energies obtained in this work are much higher than the value (0.28eV) reported for spray-deposited  $MnO_2$  thin films [25]. The high value may be attributed to better quantum confinement effect of  $MnO_2$  crystals reported here.

Table 2: Calculated energy band gap for  $MnO_2$  thin films deposited in different media.

Sample label	H2O_H2	PVA_H2	PVP_H2	H2O_H4	PVA_H4	PVP_H4
Band gap energy (eV)	2.05	2.30	1.90	1.40	1.60	1.40

The reflectivity  $R$  of materials of refractive index ( $n$ ) and extinction coefficient ( $k$ ) is given by [26,27]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (2)$$

The optical transmittance ( $T$ ) is related to the absorption coefficient ( $\alpha$ ) and the refractive index ( $n$ ) by the relation [28]:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{(1-R^2) \exp(-2\alpha d)} \quad (3)$$

The extinction coefficient ( $k$ ) is related to  $\alpha$  by the relation [26,28]:

$$k = \frac{\alpha \lambda}{4\pi} \quad (4)$$

By these relations,  $k$  and  $n$  can be defined from the measurements of  $R$  and  $T$ .

The plot of the variation of refractive index and extinction coefficient with photon energy are shown in figs. 8 and 9 respectively. Fig. 8 shows that high temperature annealing has significant influence on the refractive index of MnO<sub>2</sub> thin films. At 200°C annealing temperature, the refractive index for the films deposited in the three media have distinct values which increased uniformly to maximum values, corresponding to the visible region of the solar spectrum. Annealing the films at 400°C results to increase in the refractive index for the incident light whose energy is less than 2.0 eV. The highest observed refractive index of 2.28 was observed at photon energy of 2.99 eV (H2O\_H2), 3.88 eV (PVA\_H2), 1.43 eV (H2O\_H4), 1.65 eV (PVA\_H4) and 4.14 eV (PVP\_H4). The review of literature shows that refractive index increases with annealing temperature and this was attributed to the evaporation of water molecules off the films and subsequent formation of denser films [18].

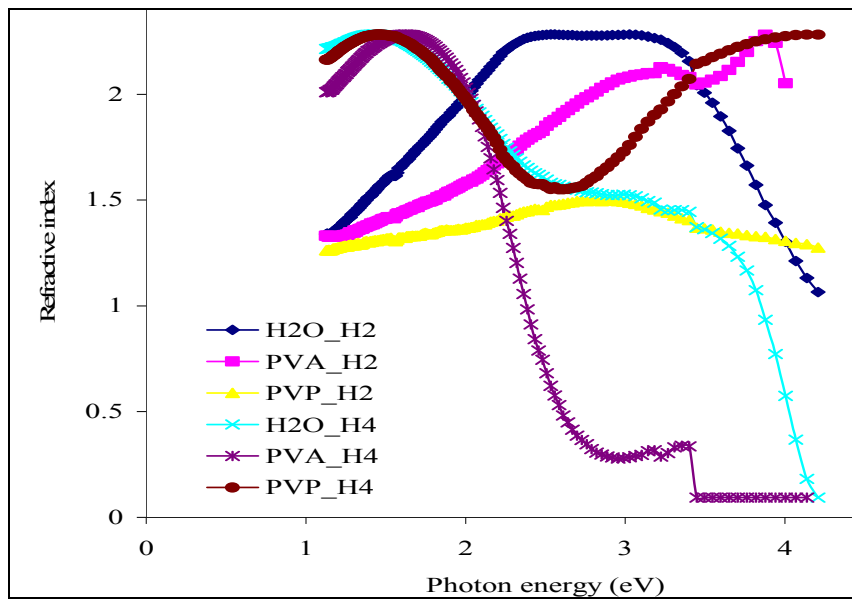


Fig.8: Refractive index vs. photon energy for MnO<sub>2</sub> thin films deposited in different media

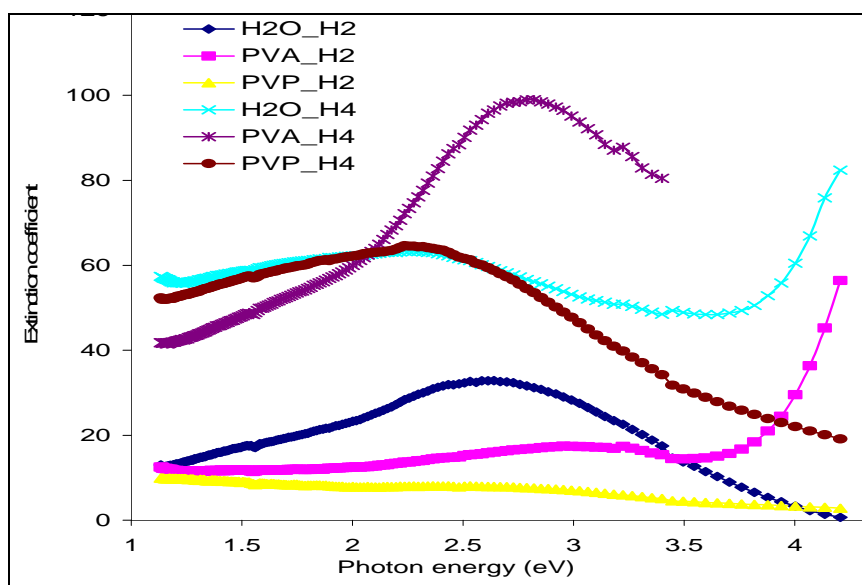


Fig.9: Extinction coefficient vs. photon energy for MnO<sub>2</sub> thin films deposited in different media

The plots of real and imaginary dielectric constant versus photon energy are shown in figs.10-11. The dielectric constants of these films are affected by the annealing temperature as well as the nature of the deposition medium. The imaginary part of the dielectric constant for the film deposited in PVP medium and annealed at 200°C decreases with the incident photon energy. Other samples have their dielectric constants increase steadily with the incident photon energy up to maximum values and then start to decrease.

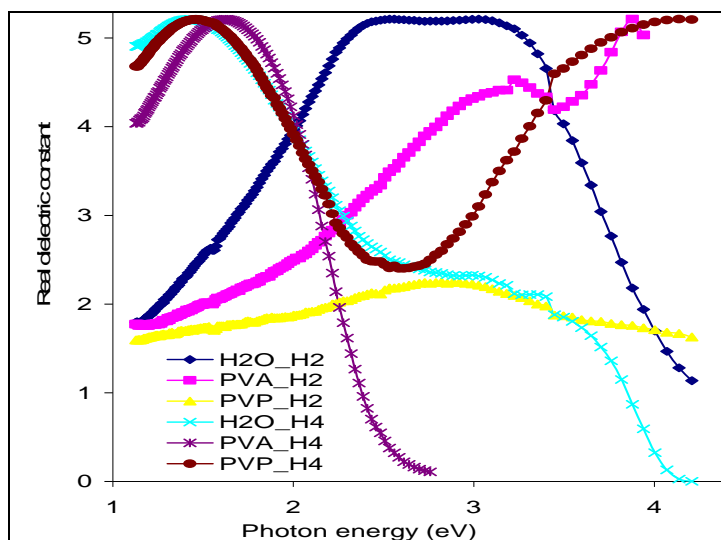


Fig.10: Real dielectric constant vs. photon energy for  $MnO_2$  thin films deposited in different media

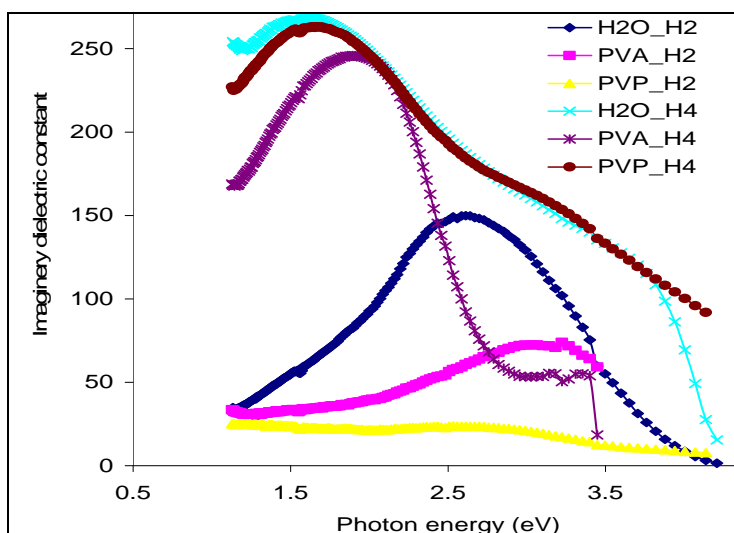


Fig.11. Imaginary dielectric constant vs. photon energy for  $MnO_2$  thin films deposited in different media

#### 4. Conclusions

Chemical bath deposition technique has been successfully used to deposit thin films of  $MnO_2$ . Their structural, composition, optical and solid state properties were studied. The XRD studies reveals that the  $MnO_2$  thin films have a preferred orientation in the (310) plane. The optical band gaps of the films lie within 1.4eV and 2.30 eV. High thermal annealing lowers the value of band gap energy of  $MnO_2$  thin films irrespective of the deposition medium. The direct band gap energies obtained in this work are much higher than the value (0.28 eV) reported for spray-

deposited MnO<sub>2</sub> thin films. The high value may be attributed to better quantum confinement effect of MnO<sub>2</sub> crystals reported here. The film deposited in PVP medium has the highest transparency in both the VIS and NIR region of the solar spectrum and is closely followed by the film deposited in PVA medium. At 200°C annealing temperature, the refractive index for the films deposited in the three media have distinct values which increased uniformly to maximum values, corresponding to the visible region of the solar spectrum. The dielectric constants of these films are affected by the annealing temperature as well as the nature of the deposition medium.

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