THE DETERMINATION OF OPTICAL BAND AND OPTICAL CONSTANTS OF MnO_2 THIN FILMS PREPARED BY SPRAY PYROLYSIS

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ABSTRACT

Polycrystal MnO_2 thin films have been deposited using spray pyrolysis deposition technique under a varied thickness. By analyzing the X-ray diffraction, the structure of deposited films was found to be polycrystalline. Different optical properties of these films have been investigated by observing the optical absorption and transmission spectra. Various optical constants such as optical energy gap, the width of band tails of localized states into the gap, and steepness parameter, were calculated and the variation of various optical parameters such as refractive index, extinction coefficient and dielectric constant, with phonon energy are estimated.

Keywords: MnO_2**,** thin films, spray pyrolysis, optical properties**.**

I. INTRODUCTION

Thin film technologies occupy a prominent place in basic research and the use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their optical electrical properties and low production costs. In the last decade, synthesis and characterization of manganese oxides in various oxidation states and in different structures have been intensified due to their promising potential for application in various fields. Manganese (IV) oxide is the inorganic compound having the chemical formula MnO_2. The principal use for MnO_2 is for dry-cell batteries such as the alkaline battery and the zinc carbon battery (Huang, et al., 2006). MnO_2 is also used as a pigment and as a precursor to other manganese compounds such as $KMnO_4$ (Greenwood and Earnshaw, 1984). It is used as a reagent in organic synthesis, for example in the oxidation of allylic alcohols, ion exchange (Tsuji, et al., 1992, Liao, et al., 2003), catalysis (Espinal, et al., 2004) and oxidation process (Fendorf and Zasoski, 1992, Tournassat, et al, 2002). A number of thin deposition methods used for the deposition of MnO_x thin films include the sol-gel method (Pang, et al, 2000, Long, et al., 2001, Giraldo et al., 2000), chemical bath deposition (Asogwa, 2010), anodic oxidation of Mn^{2+} (Chigane and Ishikawa, 2000), and spray pyrolysis (Misho et al., 1993, Al-Hamdane, et al., 2002). The spray pyrolysis method has the advantages of low cost, easy to use, safe and suitable for scientific studies and for many technological and industrial applications. Several papers reported on the production of manganese oxide thin films by spray pyrolysis and their optical properties (Misho, et al., 1993, Al-Hamdane, et al., 1998, Al-Hamdane, et al., 2002). The optical properties of Mn_2O_3,Mn_3O_4 and MnO were studied and it was found that the unfilled orbits of the transition oxides materials have optical energy gaps in the visible regional (Kim and Park, 2004).

In this work, we deposited MnO_2 thin films onto glass substrate by spray pyrolysis method, and investigate the effect of the film thickness on the optical properties, (optical band gap Urbach energy, steepness parameter, and optical constants).

II. THEORY

When one observes the optical transmittance and absorbance spectra of thin films, it is clear that the transmittance values increase with increasing wavelength and thickness of films, and absorbance decreases with increasing wavelength and thickness of films. The nature of the transition (direct or indirect) is determined by the relations (Mott and Gurney,1940)

$$\alpha h\upsilon = A(h\upsilon - E_g)^r, \qquad (1)$$

$$\alpha = \frac{\ln\left(\frac{1}{T'}\right)}{t}, \tag{2}$$

where A is a constant, $h\nu$ the photon energy, E_g the optical energy gap, α the absorption coefficient, t the thickness of the film, T' the transmittance, and r a constant which depends on the type of the electronic transitions, where r is equal to 1/2, 3/2, 2 and 3 for allowed direct, forbidden direct, indirect allowed and indirect forbidden transitions, respectively.

The absorption coefficient near the band edge shows an exponential dependence on photon energy (Urbach, 1953)

$$\alpha = \alpha_0 \exp(h\upsilon / E_u), \tag{3}$$

where α_o is a constant, and E_u is called the Urbach energy. The Urbach energy of a thin film depends on the structural defects, and dislocation density. Some defects are formed during the formation of the films, and these defects produce localized states in the band gap. The Urbach energy is interpreted as the width of the tails of localized states. Thus, a plot of ln α against $h\nu$ should be linear, and the Urbach energy can be calculated from the reciprocal slope of the linear portion.

From the Urbach energy, the steepness parameter β can be calculated using the relation (Park, 2011)

$$\beta = k_B T / U_r, \tag{4}$$

where k_B is Boltzman's constant and T is the absolute temperature. The steepness parameter characterizes the broadening of the absorption edge due to the electron-phonon interaction or excitation-phonon interaction (Dhanya and Menon, 2011).

The refractive index n and the extinction coefficient k of the sample can be obtained from the equation (Abeles, 1972)

$$n = \frac{1+R}{1-R} + [(\frac{1+R}{1-R})^2 - (k^2 - 1)]^{\frac{1}{2}}, \tag{5}$$

where

$$k = \frac{\alpha\lambda}{4\pi}. \tag{6}$$

The dielectric constant is defined as (Abeles, 1972)

$$\varepsilon = \varepsilon_r + i\varepsilon_i, \tag{7}$$

where ε_r and ε_i are the real and imaginary parts of the dielectric constant, respectively, and are related to the n and k in eqs. (5) and (6) by the relations

$$\varepsilon_r = n_2\text{-}k_2\ , \tag{8}$$

$$\varepsilon_i = 2nk. \tag{9}$$

III. EXPERIMENTAL DETAILS

MnO_2 thin films were prepared by spraying an aqueous solution of $Mn(NO_3)_2.4H_2O$ on a glass substrate kept at 300°C . Thin films with different thicknesses were obtained by varying the deposition time period. The structure of the films was analyzed using XRD technique with Cu-kα (λ= 1.54056 Å) radiation.

The transmittance and absorbance's spectrum of the films were measured by using Pye Unicom double beam spectrophotometer in the wavelength range from (300-900) nm. The substrate absorption is corrected by introducing an uncoated cleaned glass substrate in the reference beam. The thicknesses of the deposited films were 0.2, 0.35 and 0.45 μm and were measured by weight difference method.

IV. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra for MnO_2 thin films. The X-ray diffraction analysis revealed that the deposited films were polycrystalline in nature, in good agreement with those of ASTM card for polycrystalline MnO_2.

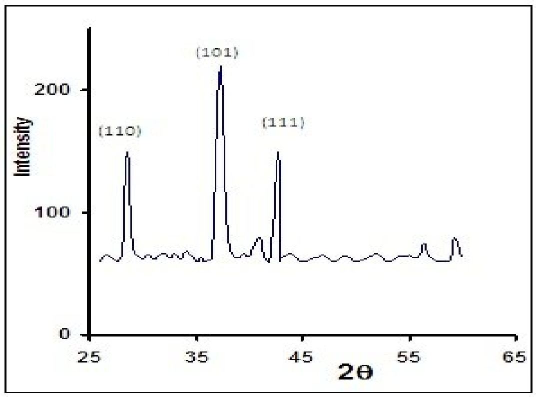

Figure 1. X-ray diffraction pattern of MnO_2 thin film.

The optical transmittance and absorbance spectra of the thin films in the UV-VS wavelength range with different thickness are shown in figures 2 and 3. It is clear that the transmittance increases with wavelength and thickness of film, while absorbance decreases with increasing wavelength and thickness of film. A plot of $(\alpha h\upsilon)^2$ against hυ is shown in figure 4. The linear nature of the graph indicates the existence of direct transitions. The values of direct optical band gap E_g were obtained by extrapolating the straight portion to the $h\upsilon$ axis at $(\alpha h\upsilon)^2 = 0$. The values of optical energy band gap obtained in this study are given in table I, and it is seen that E_g changes with thickness. The shift in the absorption energy edge from 3.4eV to 3.65 eV is a result of the so-called Burstein-Moss effect (Burstein, 1954, Moss, 1964). Ahmed, et al. (1992) calculated the value of the direct transition to be 2.8 eV. Al-Hamdane, et al. (2002) also prepared MnO_2 by spray pyrolysis method and found that the type of transition is indirect with allowed and forbidden transition energies of 1.55 eV and 1.9 eV respectively. It is concluded that the obtained optical band gap values found by this method are suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells, and piezoelectric devices. The Urbach energy is interpreted as the width of the tails of localized states. A plot of ln α against $h\nu$ should be linear, and Urbach energy was calculated from the reciprocal slope of the linear portion as shown in figure 5. The calculated Urbach energy values are listed in table I. Urbach energy values change inversely with E_g and are found to decrease with increasing thickness due to the decrease in the width of localized states in the optical band.

Table I. The optical parameters of MnO_2 thin films.

Thickness (μm)	E_g (eV)	E_u (eV)	$\beta (10^3)$
0.20	3.40	1.179	21.95
0.35	3.55	1.025	25.24
0.45	3.60	1.025	25.24

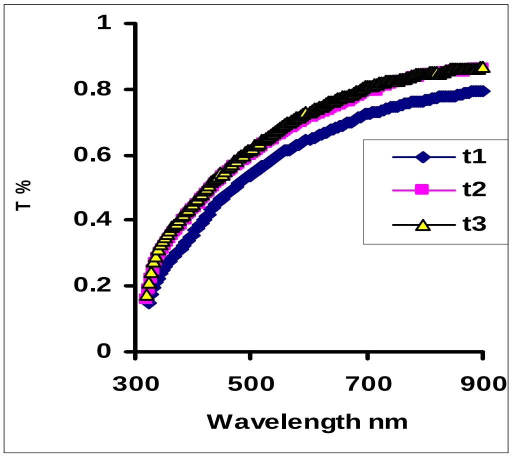

Figure 2. Optical transmission spectra.

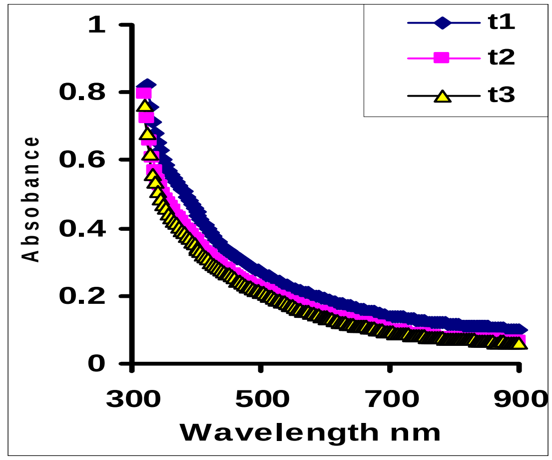

Figure 3. Optical transmission spectra.

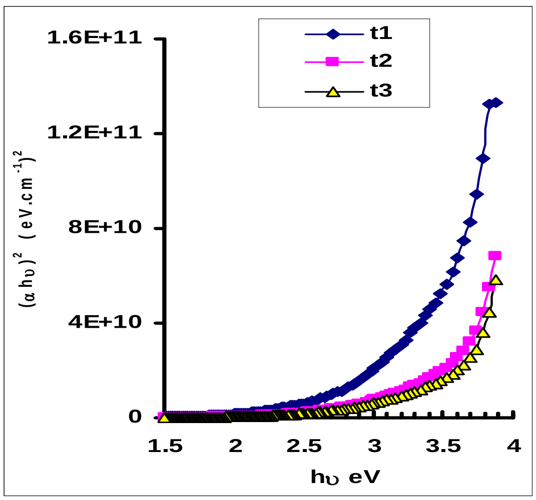

Figure 4. Plot of $(\alpha h\upsilon)^2$ against *hv*.

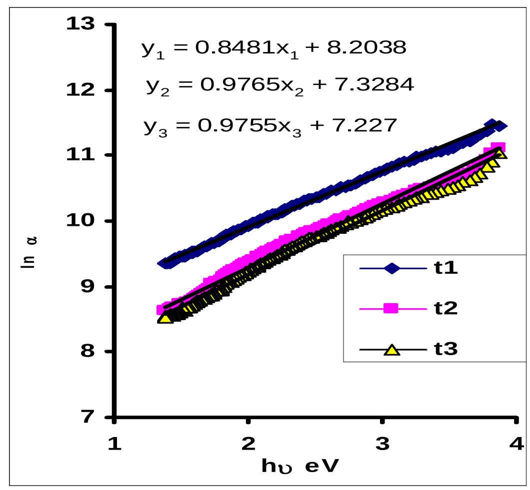

Figure 5. Plot of ln α against *hv*.

From the Urbach values, the steepness parameter β was calculated using eq. (4), and the values obtained are listed in table I. The β values suggest that the absorption edge changes with thickness.

The refractive index n and the extinction coefficient k of the sample can be obtained from eq. (5). The variation of refractive index and the extinction coefficient with wavelength and thickness are shown in figures 6 and 7, and it can be seen that the n values slightly decrease with increasing wavelength beyond the absorption edge, and decrease with increasing thickness. Accurate knowledge of the absorption coefficient, optical band gap and refractive index of semiconductor is indispensable for the design and analysis of various optical devices.

The dependence of the real and imaginary parts of dielectric constant on wavelength are shown in figures 8 and 9 for different thickness. The real part of dielectric constant follow the same pattern of refractive index and it is seen that the values of real part are higher than that the imaginary parts.

CONCLUSIONS

To summarize, MnO_2 thin films with various thicknesses were prepared by spray pyrolysis method at room substrate temperature. All the deposited films are polycrystalline in nature when film thickness is changed from 0.2 to 0.45 nm.

The optical band gap and Urbach energy change with thickness. The shift of absorption edge can be associated with the Burstein-Moss effect. The optical absorption spectra of the films under study show that direct transition is the absorption spectra mechanism, and the width of localized states decreases with increasing film thickness.

Furthermore, spray pyrolysis method is suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells, and piezoelectric devices.

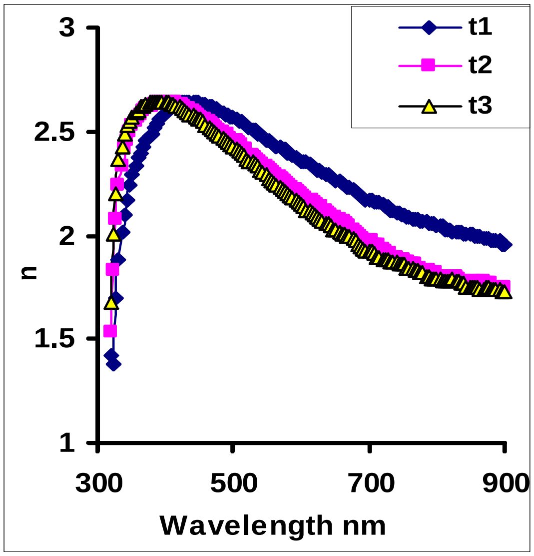

Figure 6. Variation of refractive index with wavelength.

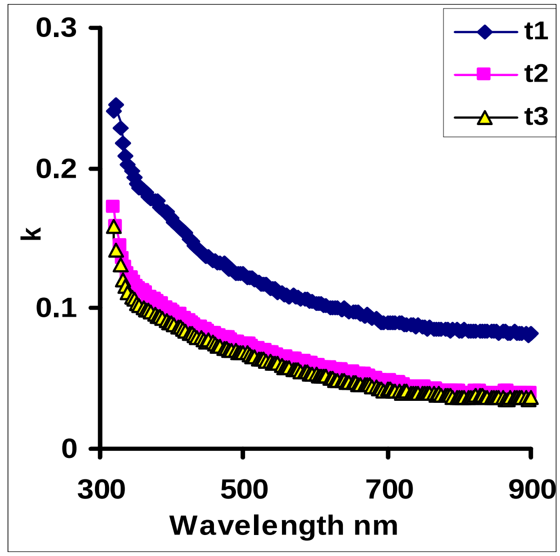

Figure 7. Variation of extinction coefficient with wavelength.

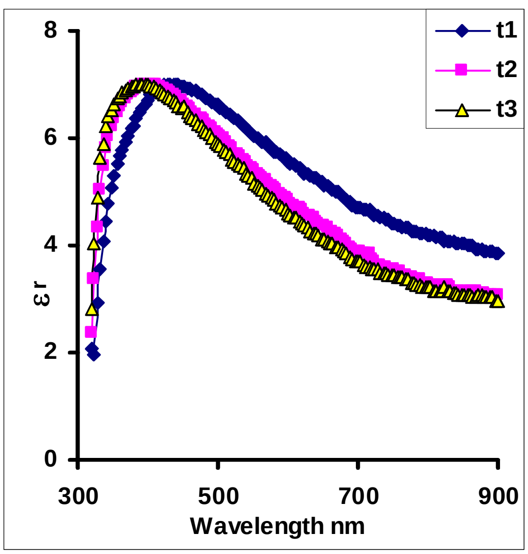

Figure 8. Variation of the real part of dielectric dielectric constant with wavelength.

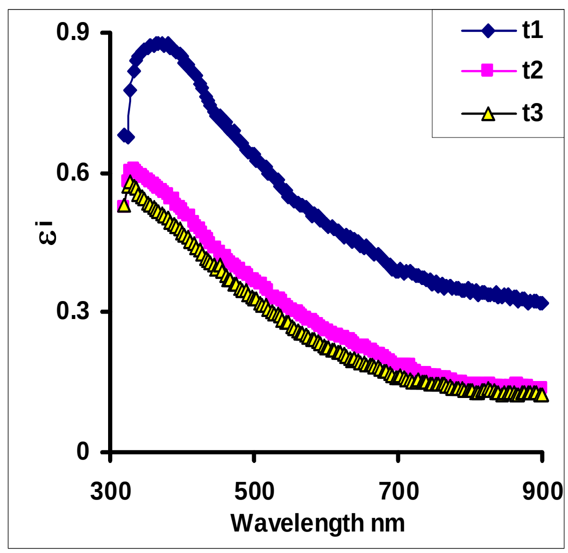

Figure 9. Variation of the the imaginary part of constant with wavelength.

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