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EFFECT OF ANNEALING TEMPERATURE ON THE DISPERSION ENERGY PARAMETERS OF SOL-GEL ROUTED MOLYBDENUM OXIDE THIN FILM

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ABSTRACT

This paper reports the influence of annealing temperature on optical and dispersion energy parameters of sol-gel routed spin – coated Molybdenum tri Oxide (MoO_3) thin films. The higher annealing temperatures increase the values of dispersion energy parameters.XRD study reveals the formation of α- orthorhombic phase at higher annealing temperature and amorphous nature at lower annealing temperature. The optical band gap of MoO_3 film is found to be 3.3 -3.8eV, and the refractive index of the film is found to be 2.2 -2.9. The dispersion curve of the refractive index shows an aberrant dispersion in the absorption region. Using the single oscillator of Wemple – Didomenico model the different dispersion energy parameters are evaluated.

INTRODUCTION

The transition metal oxide receives a considerable attention of researchers due to its wide range of optical application in the field of optoelectronics. Molybdenum tri oxide (MoO_3) is one of the transition metal oxides with a wide range of optoelectronic applications (Choi *et al*., 2012). Several deposition method such as chemical vapour deposition (Gesheva, 2003), electro deposition (Michael, 2000), electron beam deposition (Sivakumar *et al*., 2005), sputtering (Bouzidi *et al*., 2003) and spray pyrolysis (Miyata *et al*., 1985) have been used to prepare MoO_3 films. Also the sol-gel technique has been receiving high attention, as it is useful to develop high quality films at low cost with simpler deposition procedure (Aaikary and Chan, 2004). In this present work the sol-gel routed spin coating has been employed for obtaining thin film with required thickness. Prepared films were annealed atthe temperature range 250°C- 400°C and optical dispersion energy parameters have been investigated. The novelty of the present work is to study the effect of annealing on the dispersion energy parameters of MoO_3 thin film.

MATERIALS AND METHODS

Sol-gel routed spin coating technique has been employed to prepare the MoO_3 thin film.

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Ammonium Molybdatehepta hydrate (99.98%, Sigma Aldrich, USA) was preheated at 275° C. The precursor solution was prepared by dissolving 0.435g of preheated Ammonium Molybdatehepta hydrate in 50 ml of 2-Methoxyethanol.A few drops of conc. HCL were added to the solution and stirred at 80° C for 2 hours. The prepared sol was converted into film by spin coating technique. The MoO_3 film was coated on the FTO substrate at 3000 rpm by keeping the spinning time as 60 seconds at normal atmospheric condition. Film was coated as multiple layers to obtain the required thickness. After each layer of coating the film was dried at 100° C for 5 minutes. The films were annealed at the temperature range 250° C–400° C for 2 hours by keeping the rate of temperature at 4° C per minute. The thickness of the film was measured by stylus profilometer (Mitutoyo, SJ-301). The X- ray diffraction for phase identification was performed using XPERT-PRO X-ray diffractometer with Cu-K_α (λ=0.154nm) radiation source. The optical characterization was done by using Perkin Elmer Lambda - 35 UV-Visible spectrometer.

RESULTS AND DISCUSSION

Structural property

The Molybdenum oxide thin films of thickness 3μm are prepared and annealed at temperatures 250° C, 350° C and 400° C.The XRD pattern of MoO_3 thin film (Fig.1) exhibits amorphous nature for the film annealed at 250° C and crystalline nature for the film annealed at 350° C and 400° C. The films are annealed at 400° C exhibit α- orthorhombic phase with preferential orientation along (0 2 0) plane (JCPDS Card No. 89- 5108) (Dhanasankar *et al*., 2011). The peak intensity increases with increase of temperature and it may be due to the increase in grain size of the crystal lattice (Kassim *et al*., 2010).

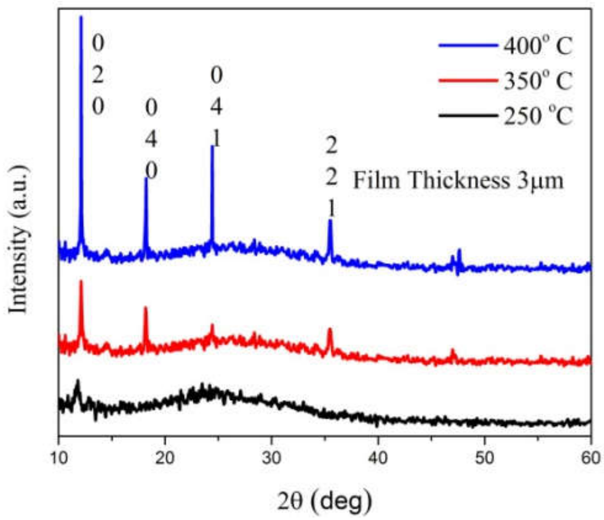

Fig. 1. XRD pattern of MoO_3 thin film

Optical Constants

The optical transmission spectra of MoO_3 films annealed at various temperatures exhibit good transparency at 570 nm (Fig.2). The film annealed at 250° C exhibits maximum transparency of 80 %. The transparency of the film decreases with increase of the annealing temperature. The film annealed at 400° C exhibits only 60% of transparency at 570 nm that might be due to the free carrier absorption and formation of micro crystallites leading to the scattering of light (Tate, 1991 and Eswaramoorthi, 2014). The higher transmittancein the higher wave length region indicates the reduction in optical band gap (E_g) with increase of the annealing temperatures (Sivakumar *et al*., 2004). From the transmission spectrum the absorption coefficient (α) is determined by the relation (Antony *et al*., 2007).

$$\alpha = \frac{1}{t}\ln T \qquad \text{..................(1)}$$

where t is thickness of the film and T is transmittance. The band gap of the film is determined from the relation (Pankove, 1971)

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\upsilon - E_g) \qquad \text{.................(2)}$$

A is the energy dependent constant, E_g optical band gap energy of the material and n = ½, 2, 3/2, 3 corresponding to the allowed direct, allowed indirect and forbidden direct and forbidden indirect transitions respectively. The optical band gap depends upon the absorption coefficient (α). The MoO_3 is found to be direct band gap material (n= 1/2). The extrapolation of linear portion (α=0) gives the optical band gap energy of the film. Fig. 3 shows the plot of $(\alpha h\upsilon)^2$vs hυ for MoO_3at different annealing temperature. It reveals that the optical band gap of the MoO_3 film decreases with increase of the annealing temperature that might be due to formation of oxygen ion vacancies in the film during the annealing (Anwar *et al*., 1989). The optical band gap value of MoO_3 film at 250° C, 350° C and 400° C are 3.8, 3.5and 3.3eV respectively.

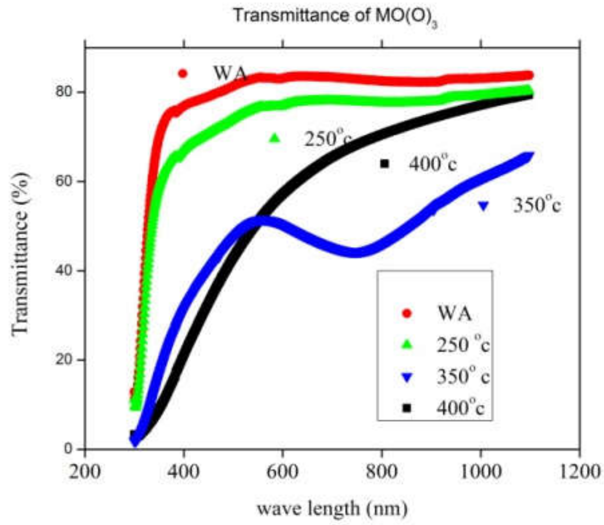

Fig. 2. Transmittance spectrum of MoO_3 film

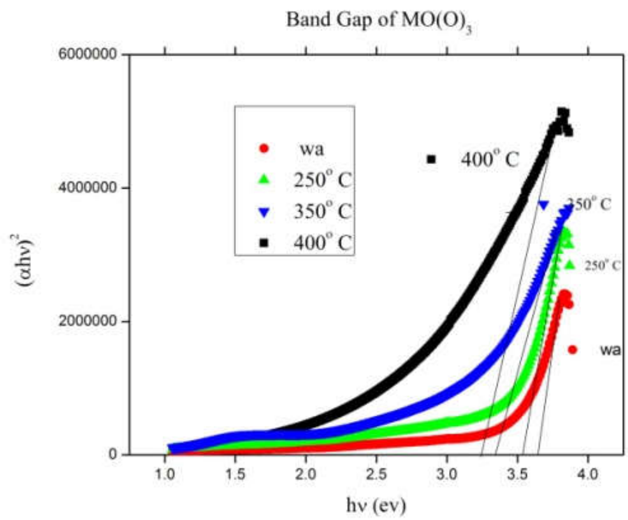

Fig. 3. Band gap of MoO_3 film

Refractive index and Extinction coefficient

When the electromagnetic wave propagates through a lossy medium, it will have some attenuation. It is owing to the loss occurred by generation of phonons and photons, free carrier absorption and scattering (Usha *et al*., 2013). In such materials, refractive index becomes a complex function of frequency of electromagnetic wave. The refractive index and extinction coefficient are calculated from the relations (Subrahamanyam *et al*., 1977):

$$n = \left(\frac{1+R}{1-R}\right) - \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad \text{....................(3)}$$

$$k = \frac{\alpha\lambda}{4\pi} \qquad \text{.....................(4)}$$

Where R is the reflectance of the film and λ is wave length of the incident beam. The refractive index decreases with increase of the wave length and increases with increase of the annealing temperature (Fig.4). This would be due to the densification of the film by annealing (Cimalla *et al*., 2014). The extinction coefficient increases with increase of the annealing temperature (Fig. 5).

The MoO_3 film exhibits low value of extinction coefficient at the visible region that indicates the surface homogeneity of MoO_3film (Tigau *et al*., 2005). The increment of k with annealing temperature might be due to the raising of surface roughness (Safwat *et al*., 2011). Generally the refractive index is higher for shorter wavelength and it decreases gradually at higher wavelength. Some highly colored materials have abnormal dispersion. This is due to strong absorption at higher wavelength region (Safwat *et al*., 2011). The films annealed at250° C and 400° C exhibit the normal dispersion and the film annealed at the 350° C exhibits abnormal dispersion at the wave length of 750-800nm (Fig.4) that might be due to more absorption at those wave length region (Cimalla *et al*., 2014).

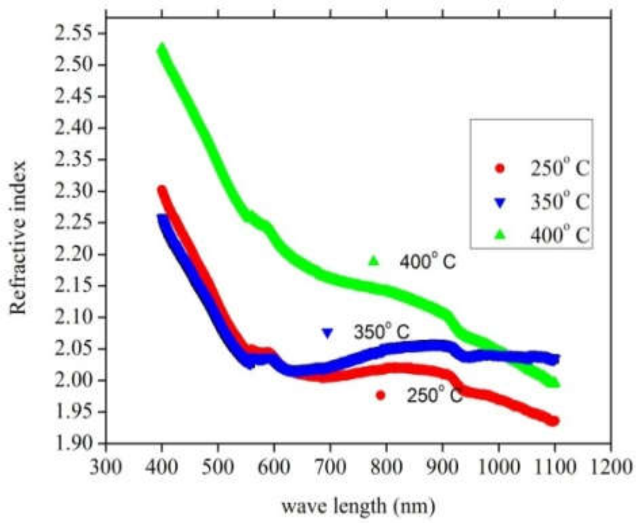

Fig. 4. Refractive index of MoO_3 thin film

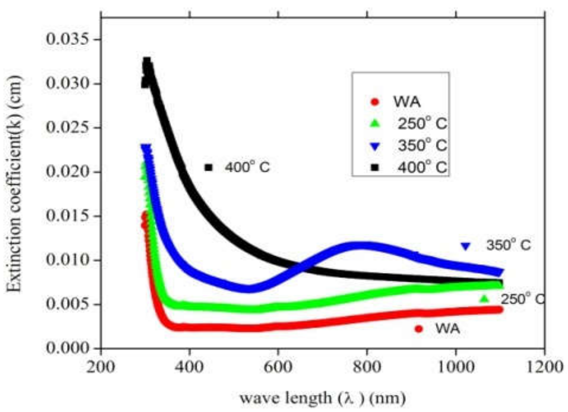

Fig. 5. Extinction coefficient of MoO_3 thin film

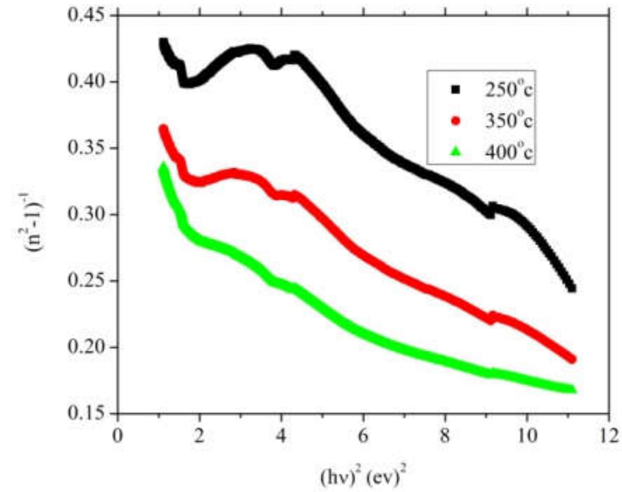

Fig. 6. $(n^2-1)^{-1}$vs $(h\upsilon)^2$

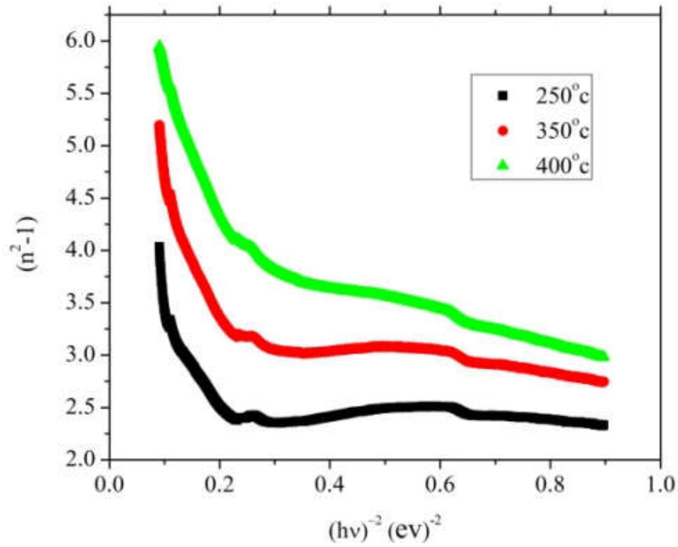

Fig. 7. (n^2-1) vs $(h\upsilon)^{-2}$

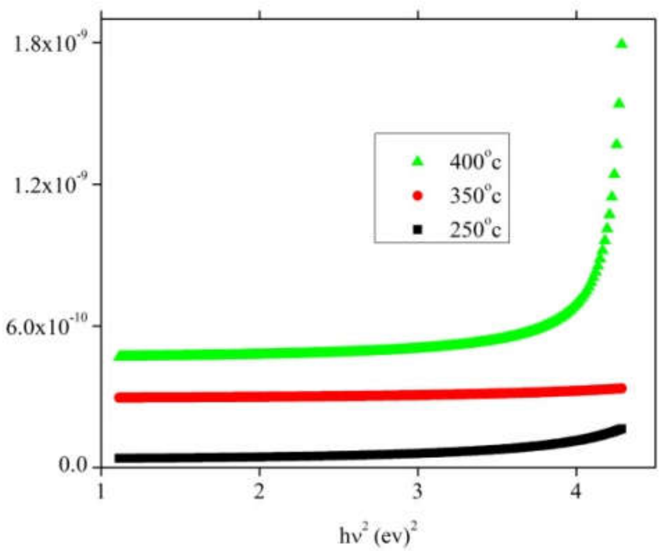

Fig. 8. Optical susceptibility

Table 1.

Annealing temperature (°C)	E_0(ev)	E_d(ev)	E_l(ev)	E_g(ev)	E_0/E_g	N_c	n_0
250	5.69	12.85	0.73	3.8	1.31	8.24	1.83
350	4.86	13.24	1.59	3.5	1.40	8.49	1.90
400	4.35	13.42	2.78	3.3	1.50	8.60	2.05

Oscillator Energy (E_0), Dispersion Energy(E_d), Lattice Energy (E_l) Optical band gap (E_g) coordination factor (N_c), Static Refractive index (n_0)

The refractive index and absorption coefficient are atomic-density dependent parameters. The refractive index of crystalline materials is higher than the amorphous material. Hence, the crystalline nature of MoO_3 films annealed at 350° C and 400° C exhibit high n and k values.

Dispersion energy parameter

The dispersion energy parameter plays a crucial role in the optical materials like MoO_3 for their immense application in designing the device for spectral dispersion and optical communication. The dispersion energy parameters have been extracted from the Wample and Didemenico (WD) model (Wemple *et al*., 1971). According to this model, the dispersion energy parameters E_d and E_o are defined by the single oscillator description of frequency dependent dielectric constant. The refractive index can be expressed by the Selmeier relation (Wemple, 1971).

$$n^2 - 1 = \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(5)$$

where E_0 is the average oscillator energy (an average of the optical band gap) and E_d is the dispersion energy parameter of a material. It can give the average strength of inter band optical transition. The E_d and E_0 values obtained from the graph (Fig.6)plotted between $(n^2\text{-}1)^{-1}$ and (hυ), ^{2}the value of E_d is the 'y' intercept, and the slope of the graph is E_0.The oscillator energy E_0 decreases with increasing the annealing temperature. It might be due to the increase in the number of scattering center and also due to the decrease in band gap energy. The increase in the value of $E_d$with increasing the annealing temperature attributed to the increase in the co ordination number of atom (Madhup, 2010). As suggested by WD model E_0 = 1.5 E_g. From the Table.1,the films annealed at 400°C have a good agreement with this WD model suggestion (Wemple *et al*., 1971).

The wimple Dedominico model relates the dispersion energy with other physical parameters of the materials from the relation (Wemple *et al*., 1971; Madhup *et al*., 2010 and Wemple *et al*., 1973).

$$E_d = \beta N_c Z_a N_e (eV) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Where β is the two valued coordination factor which either ionic (β_i =0.26±0.03 eV) or covalent (β_c =0.31±0.04 eV), $N_c$is the coordination number of the cation nearest number to the anion, Z_a is the formal chemical valency of the anion,N_e is the total number of valence electron per anion. Since the MoO_3 is ionic in nature the β_i = 0.26, Z_a=1,N_e=6. The calculated coordination number (N_c) is found to increase with increase of annealing temperature (Table 1). The increment in $N_c$supports the hypothesis of dispersion energy parameter E_d. The optical parameters E_0 and E_d can be related with the lattice energy E_l. The lattice energy gives the information about bonding in the ionic compounds. The E_l can be evaluated from the relation (Wample *et al*., 1979).

$$n^2 - 1 = \left(\frac{E_d}{E_0}\right) - \left(\frac{E_l^2}{E^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots..(7)$$

From this relation the lattice energy can be obtained by plotting the graphbetween $(n^2\text{-}1)$ and $h\upsilon^{-1}$ (Fig. 7). The slope value of the graph gives the $-E_l$. The lattice energy increases with increase of the annealing temperature which shows the enhancement in the strength of the bonds (Wample *et al*., 1979). Using these dispersion energy parameters the static refractive index (Zero frequency refractive index) can be calculated from the relation (El-Sayed *et al*., 2004).

$$n_0^2 = 1 + \frac{E_d}{E_0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

The n_0 value increases with increase of annealing temperature (Table:1), it might be due to densification of the film due to annealing.The third order optical non linear susceptibility ($\chi^{(3)}$) can be calculated from the dispersion energy parameter. The non linear susceptibility can give the information about the chemical bond between the molecules of the MoO_3 thin films (Al-Ghamdi *et al*., 2009). The $\chi^{(3)}$ value can be obtained from the relation (Wagner *et al*., 2003).

$$\chi^{(3)} = A \frac{E_0 E_d}{4\pi\left[E_0^2 - (h\nu)^2\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

Where A is the constant, A=1.7 x 10^{-10}esu. The non linear susceptibility increases with increasing the photonic energy and annealing temperature (Fig. 8). It reveals that the annealing increases the strength of the chemical bond between the molecules.

Conclusion

The effect of annealing temperature on optical and dispersion energy parameters of sol- gel routed molybdenum oxide thin film has been investigated. The crystallinity of the film has been enhanced by increase of the annealing temperature. The films that are annealed at 350°C and 400°C exhibit α-orthorhombic phase with preferential orientation along the (0 2 0) plane. The optical parameters of molybdenum oxide thin film have been improved by the annealing temperature. The heat treatment reduces the band gap of MoO_3 from 3.8 to 3.3 eV. The different Dispersion energy parameters have been determined through the refractive index.

The dispersion energy parameters increase with increase of annealing temperature. Using the dispersion energy parameter other optical and physical parameters like the coordination factor, lattice energy, static refractive index and optical susceptibility have been evaluated. The calculated values of optical parameters will be useful for standardizing the MoO_3 film for different optoelectronic applications.

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