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Optical Properties of Vacuum Evaporated WO_3 Thin Films

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Abstract

Thin films of WO_3 were prepared by vacuum evaporation technique in the temperature range 303-603 K. The deposition parameters such as substrate temperature, deposition rate, film –substrate combination, vacuum during the film deposition were controlled. The influence of substrate temperature on the optical properties of WO_3 films has been studied in the wavelength range 300-1600 nm. The optical band gap is found to be dependent of the deposition temperature and decreased from 3.18 to 2.90 eV with increase of deposition temperature from 303 to 503 K. The effect of heat treatment in air (calcination) on the optical properties of the films is also reported.

Key words: WO_3 thin films, vacuum evaporation, optical properties, band gap, refractive index.

Introduction

In the last several decades, many transition metal oxides have been exploited in many challenging fields of information science, nano and micro-electronics, computer science, energy, transportation, safety engineering, military technologies, opto-electronic, electrochromic devices etc. Among transition metal oxides, tungsten trioxide (WO_3) is one of the most interesting materials exhibiting a wide variety of novel properties particularly in thin film form useful for advanced technological applications. It exhibits structural transformations and sub-stoichiometric phase transitions, which attracted the attention of researchers over the past few years to explore their potential scientific and technological applications in the fields of display systems and microelectronics[1,2]. It exhibits electrochromic properties which make it suitable for variable reflection mirrors, dazzle free mirrors in automobiles, variable sun protection system usually called 'smart window' (variable transmittance) and surfaces with tunable emittance of thermal control of satellites. It has been recognized as a significant chromic material that can be colored through electro-, photo-, gas-, laser- and thermochromism processes[3].

Tungsten trioxide exhibits a cubic perovskite like structure based on the corner sharing of regular octahedra with the oxygen atoms at the corner and the tungsten atoms at the center of each octahedron. The crystal network is the result of alternating disposition of O and WO_2 planes normally to each main crystallographic direction. Actually, the symmetry of WO_3 is lowered from the ideal ReO_3 structure by two distortions: tilting of WO_6 octahedra and displacement of tungsten from center of its octahedron [4].

Tungsten trioxide can be deposited in thin film from using various deposition techniques and finds their effective use in scientific and technological applications. Recently thin film WO_3 has been received a growing interest and concern with respect to its excellent gas-chromatic properties and has been established as one of the best gas sensors for the reducing gases. Tungsten trioxide thin films have been deposited by a number of deposition techniques such as thermal evaporation[5], electron beam evaporation[6], chemical vapor deposition[7], laser deposition[8]. Each deposition technique produced different properties on different substrates in terms of composition, structure and morphology [8]. It is required that the thin film deposition technique should satisfy certain criteria of producing thin films with properties such as well adherence, pin hole free, stoichiometric, films with good crystallinity at lower substrate temperatures.

Thermal evaporation is one of the most widely used, simplest and convenient techniques for the deposition of thin films. In this technique, the material can be evaporated by means of resistive heating or rf heating. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and to reduce the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapour pressure than the heating element can be deposited without contamination of the film. The material has to be evaporated in vacuum environment which comprises of a diffusion pump backed by a rotary pump. A sufficient amount of heat must be supplied to the evaporant to attain the vapor pressure necessary for evaporation. The evaporated material is allowed to condense onto a substrate kept at a suitable temperature. A container which supports the evaporant and supplies the heat of

vaporization is called a source material. To avoid contamination of the deposited film, the source material must have negligible vapor and dissociation pressures and also high melting point at the operating temperatures. Various types of sources are available to evaporate different materials. Initial stages of WO_3 growth on silicon substrates using thermal evaporation technique was studied by Ottaviano et al.[9]. The films were deposited under high vacuum conditions (10^{-6} Torr) with various (5 nm, 10 nm and 20 nm) thicknesses. The effect of annealing on the structural and optical properties of WO_3 thin films prepared by electron-beam evaporation technique was investigated by Joraid et al.[6]. However the investigations on the optical properties of WO_3 thin films that are essentially depend upon the deposition parameters give a scope for effective utilization of these thin films in the device application. Hence in the present study the influence of deposition parameters on the optical properties of vacuum deposited WO_3 thin films were reported.

Material and Methods

Tungsten oxide thin films were prepared on to Corning 7059 glass substrates by thermal evaporation of pure WO_3 Powder (purity 99.99% obtained from MERCK) from an electrical heated molybdenum boat kept at ~ 1823 K in a vacuum better than 8 x 10^{-6} Torr. A Hind High Vacuum 12A4 Coating unit was used for the deposition of the experimental films. A diffusion pump backed by a rotary pump was employed to produce the ultimate pressure of 3 x 10^{-6} Torr. Well cleaned Corning 7059 glass substrate along with suitable masks were mounted on a copper holder which was fixed on a tripod in the beljar. The source to substrate distance was fixed at 15 cm. After getting the ultimate vacuum of 5 x 10^{-6} Torr and the desired substrate temperature in the chamber, the glow discharge was initiated further ionically clean the substrates in the vacuum chamber. This was done for about two minutes. The system was allowed to reach the ultimate vacuum. When the power was fed to the boat, the material in the boat evaporated and the vapours reacted with the oxygen gas leading to film deposition on the substrate. The deposition temperature was in the range of 303 - 603 K, and it was measured by a Chromel- Alumel thermocouple attached to the substrate and precisely controlled by a temperature controller. The temperature of the boat during deposition was monitored by means of an optical pyrometer[10].

The substrates were maintained at the required deposition temperature and then, the molybdenum boat in which WO_3 powder was kept, was heated slowly. The shutter covering the substrates was opened when the temperature of the boat reached about 1823 K and it was maintained during the deposition of the films. The deposition rate observed by a quartz crystal thickness monitor was 10 A^0/sec. The thickness of the films investigated was about 4000 A^0. The optical transmission and reflectance were recorded using Hitachi U 3400 UV-VIS- NIR double beam spectrophotometer in the wavelength range 300-1600 nm, for WO_3 films deposited on glass substrates to determine the band gap and the influence of substrate temperature on the optical band gap and refractive indices of the deposited films.

Results and Discussion

The deposition parameters such as substrate temperature, deposition rate, film –substrate combination, vacuum during the film deposition etc. greatly influence the physical and chemical properties of the oxide thin films. In the present investigation thin films of WO_3 were prepared on Corning 7059 glass substrates keeping all the deposition parameters fixed except the substrate temperature. WO_3 films formed at Ts < 403K were found to be translucent white. The color of the films changed to pale blue and then to deep blue with increasing deposition temperature.

Optical Properties: The optical transmission spectra of the films deposited at different substrate temperatures are shown in figure-1. The fundamental absorption edge was observed for an incident photon wavelength of about 400 nm with a broad absorption band around 900 nm. The films formed at room temperature show high optical transmission without significant broad band absorption. The optical transmission above the fundamental absorption edge decreased with increasing deposition temperature and a slight shift in the absorption edge towards to higher wavelength region was observed.

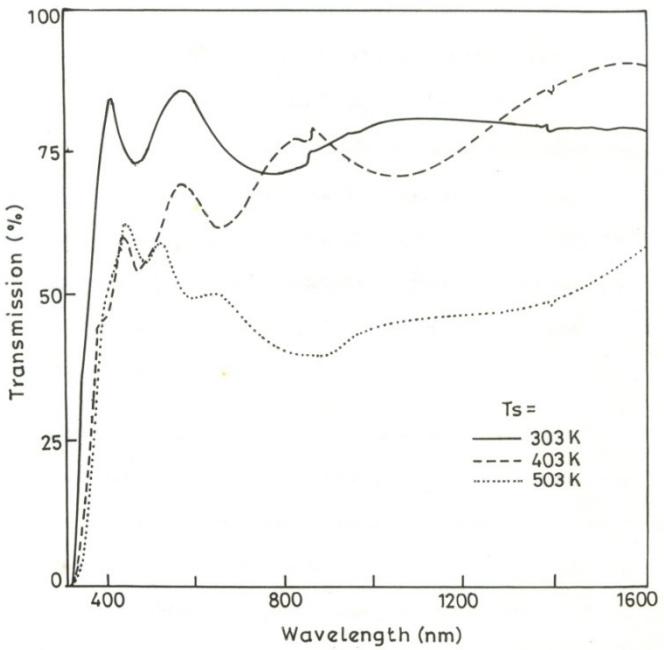

Figure-1
The optical transmission spectra of WO_3 thin films formed at various deposition temperatures

The optical absorption coefficient (α) was evaluated from the relation,

$\alpha = [l/t] \ln[T/(l-R)^2]$ ---------- (1)

Where 'T' is the transmittance 'R' the reflectance and 't' the film thickness. The optical band gap of the film was evaluated from the absorption coefficient by fitting the data to the relation

$(\alpha h\upsilon) = \beta (h\upsilon - Eg)^n$ ----------(2)

Where hυ is the incident photon energy, 'β' the edgewidth parameter and 'n' the exponent. The exponent (n) determines the type of electron transition causing the absorption, and can take values of '1/2' for direct allowed, '3/2' for direct forbidden, '2' for indirect allowed and '3' for indirect transitions.

The optical band gap of the films deposited at various substrate temperatures was obtained from the absorption coefficient data. The photon energy dependence of 'α' in the region of absorption edge ($\alpha \geq 10^4$ cm $^{-1}$) was found to fit to the relation $(\alpha h\upsilon) = \beta (h\upsilon - E_g)^2$. Hence a plot of $(\alpha h\upsilon)^{1/2}$ vs hυ should be linear and the intercept of the line on the abscissa at $(\alpha h\upsilon)^{1/2}$ = O yields the optical band gap E_g. Figure-2 shows the plots of $(\alpha h\upsilon)^{1/2}$ vs hυ for the films formed at different deposition temperatures. The linear variation of $(\alpha h\upsilon)^{1/2}$ vs hυ indicated that the transition is indirect allowed. The evaluated band gap for the films deposited at room temperature was 3.18 eV and is in good agreement with the value reported in literature[11]. The optical band gap deduced from the plots are found to be dependent of the deposition temperature and decreased from 3.18 to 2.90 eV with increase of deposition temperature from 303 to 503 K.

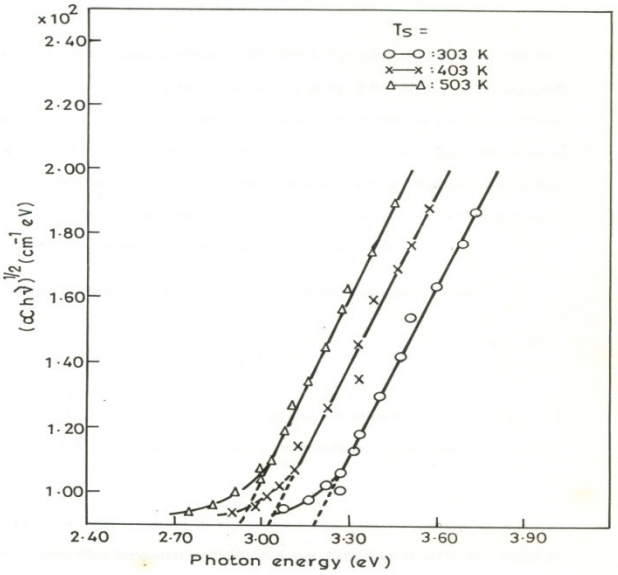

Figure-2
The plots of $(\alpha h\upsilon)^{1/2}$ vs hυ of WO_3 thin films formed at various deposition temperatures

The decrease of the optical band gap and increase in the absorption in the near infrared region with increasing deposition temperature may be due to the formation of oxygen vacancies. The results of optical studies revealed that the films formed at room temperature are nearly stoichiometric, where as those formed at elevated temperature are substoichiometric WO_{3-y}, where 'y' is a small fraction.

This substoichiometric WO_{3-y} contains a large number of oxygen ion vacancies which act as positive structural defects. These defects form a donor level below the conduction band and are responsible for the broad band absorption around 900 nm. This near infrared broad band absorption was also observed by Miyake et al.[10] for thermally evaporated films. The concentration of positive structural defects increases with increase in deposition temperature and lowers the band gap of the films.

The optical transmission spectra of the films deposited at T_s ~ 503K and heat treated in air at 673 K for about six hours are shown in figure-3. This spectrum indicates a high transmission of the films without significant absorption in the near infrared region. The evaluated band gap from the plots of $(\alpha h\upsilon)^{1/2}$ vs hυ (figure- 4) is about 3.22 eV which is in good agreement with the reported value on tungsten oxide thin films[10]. The increase in transmission and band gap of the films after heat treatment in air is attributed to the partial filling up of oxygen ion vacancies.

Refractive index: The refractive index (n) of the films was calculated from the relation

$$n^2 = \frac{n_a^2 + n_g^2}{2} + 2n_a n_g T_0 + \left(\left[\frac{n_a^2 + n_g^2}{2} + 2n_a n_g T_0 \right]^2 - n_a^2 n_g^2 \right)^{\frac{1}{2}}$$

-------(3)

Where $T_0 = (T_{max} - T_{min}) / T_{max} T_{min}$, n_a and n_g are the refractive indices of air and glass, and T_{max} and T_{min} are the consecutive transmittances maxima and minima respectively.

Figure-5 shows the variation of refractive index with wavelength of air heat treated tungsten oxide film deposited at 503 K. A large dispersion in refractive index is observed in the short wavelength region i.e. 400 to 600 nm and above 600 nm the refractive index is nearly constant. The refractive index above 600 nm was about 2.1 which is in good agreement with the reported value for stoichiometric tungsten oxide films.

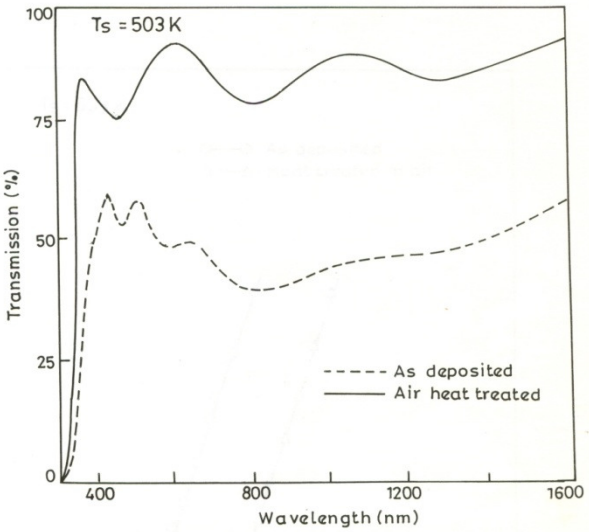

Figure-3
The optical transmission spectra of WO_3 thin films formed at 503 K and heat treated film in air at 673 K

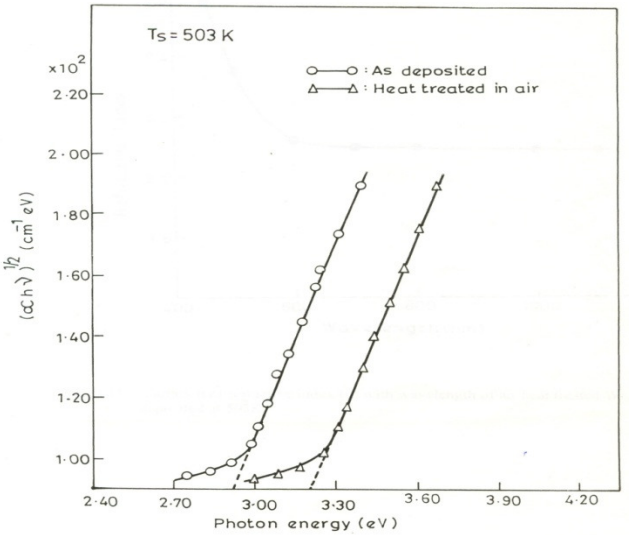

Figure-4
The plots of $(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$ of WO_3 thin films formed at 503 K and heat treated film in air at 673 K

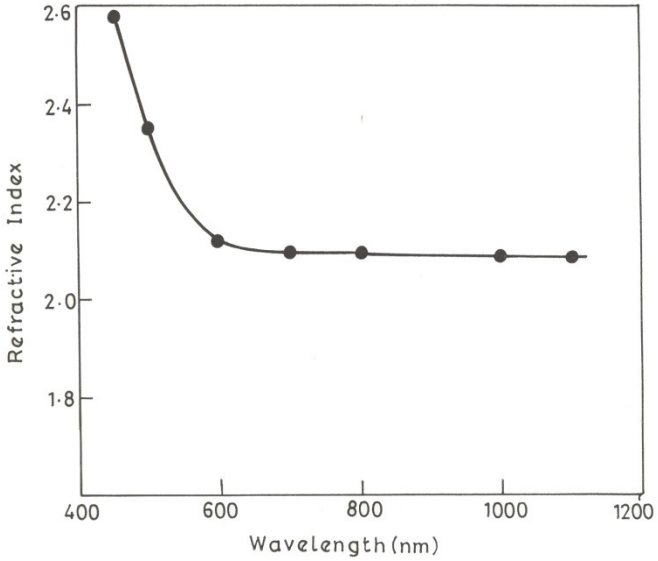

Figure- 5
Variation of refractive index (n) with wavelength of air heat treated WO_3 thin film deposited at 503 K

Conclusions

WO_3 thin films were prepared by vacuum evaporation technique in the temperature range 303-603 K. The influence of substrate temperature on the optical properties of WO_3 films has been studied in the wavelength range 300-1600 nm. The optical band gap is found to be dependent of the deposition temperature and decreased from 3.18 to 2.90 eV with increase of deposition temperature from 303 to 503 K. The decrease of the optical band gap and increase in the absorption in the near infrared region with increasing deposition temperature may be due to the formation of oxygen vacancies. The effect of heat treatment in air (calcination) on the optical properties of the films is also clearly evidenced. The increase in transmission and band gap of the films after heat treatment in air is attributed to the partial filling up of oxygen ion vacancies. These substoichiometric WO_3 films can be utilized in electrochromic devices and in solid state microbatteries.

References

1. Arof A.K., Saniman E.B. and Mastor M.Z., Some properties of Agl-Ag_2O-MoO_3 electrolyte doped with Al_2O_3, *J. Phys. III France,* **4**, 849-858 (**1994**)

2. Granqvist C.G., Electrochromic tungsten oxide films: Review of progress 1993- 1998, *Solar Energy Materials and Solar Cells,* **60**, 201-262 (**2000**)

3. Ashrit P.V., Bader G. and Truong V.V., Novel electrochromic devices based on complementary nanocrystallineTiO_2 and WO_3 thin films, *Thin Solid Films,* **320**, 324-329 (**1998**)

4. Woodward P.M., Sleight A.W. and Vogt T., Ferroelectric tungsten trioxide, *J. Sol. State Chem.,* **131**, 9-17 (**1997**)

5. Antonaia A., Polichetti T., Addonizio M.L., Aprea S., Minarini C. and Rubino A., Modification of vapor-deposited WO_3 electrochromic films by oxygen backfilling, *Thin Solid Films,* **354**, 73-81 (**1999**)

6. Joraid A.A. and Almari S.N., Effect of annealing on structural and optical properties of WO_3 thin films prepared by electron-beam coating, *Physica B: Physics of Condensed Matter,* **391,** 199-205 **(**2007**)**

7. Tagtstrom P. and Jansson U., Chemical vapour deposition of epitaxial WO_3 films, *Thin Solid Films*, **352,** 107-113 **(1999)**

8. Hussain O.M., Swapnasmitha A. S., John J. and Pinto R., Structure and morphology of laser-ablated WO_3 thin films, *Appl. Phys. A*, **81**, 1291-1297(**2005**)

9. Ottaviano L., Rossi M. and Santucci S., Initial stages of WO_3 growth on silicon substrates, *Thin Solid Films,* **490,** 59-67 **(2005)**

10. Rao M.C., Effect of substrate temperature on the structural and electrical conduction behaviour of vacuum evaporated WO_3 thin films, *J. Optoelect. & Biomedical Mater.,* **3,** 45-50 (**2011**)

11. Miyake K., Kaneko H., Sano M. and Suedomi N., Physical and electrochromic properties of the amorphous and crystalline tungsten oxide thick films prepared under reducing atmosphere, *J. Appl. Phys*., **55**, 2747-2753 (**1984**)