EFFECT OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL AND ELECTRICAL CONDUCTION BEHAVIOUR OF VACUUM EVAPORATED WO_3 THIN FILMS

M. C. RAO[*]
Department of Physics, Andhra Loyola College, Vijayawada – 520008, India

WO_3 thin films were prepared by vacuum evaporation technique. 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 structural and electrical properties of WO_3 films has been studied. The WO_3 films deposited at Ts ~ 503 K and subsequently annealed at 673 K for 6 hours in air showed characteristic (020), (021), (002) orientations representing the orthorhombic phase of WO_3. The influence of substrate temperature on the electrical properties of WO_3 films has been studied. The conductivity was found to increase with increasing substrate temperature and the increase was more predominant for the films formed at $T_s > 453$ K. The increase in conductivity is mainly due to the oxygen ion vacancies formed in the films during the deposition due to the partial dissociation of constituent elements. The WO_3 films formed at 303 – 503 K and subsequently calcinated at 673 K for six hours were found to be translucent white. The electrical conductivity of these films was in the range 8×10^{-8} to 4×10^{-7} ohm^{-1} cm^{-1}.

(Received May 26, 2011; Accepted June 10, 2011)

Keywords: WO_3 thin films, Vacuum evaporation, Structure, Electrical properties

1. Introduction

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 [1-4]. 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 [5-7]. WO_3 being an n-type semiconductor exhibits novel electronic properties and it has been considered as a potential candidate for sensing pollutant gases like NO_x, NH_3, CO, H_2S etc. It is also used as a catalyst, window for solar cells and low voltage varistors.

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 [8]. Thus variations from these crystallographic distortions, WO_3

---

[*] Corresponding author: raomc72@gmail.com

exhibits structural transformations and undergoes at least five equilibrium phase transformations in a sequence:
tetragonal→ orthorhombic→ monoclinic→ triclinic→ monoclinic, when the temperature is decreased from the melting point [9].

Tungsten trioxide can be deposited in thin film form 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 [10, 11], electron beam evaporation [12, 13], chemical vapor deposition [14, 15], sputtering [16, 17], sol-gel [18], spray pyrolysis [19, 20]. Each deposition technique produced different properties on different substrates in terms of composition, structure and morphology [19, 20]. 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 technique 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. Initial stages of WO_3 growth on silicon substrates using thermal evaporation technique was studied by Ottaviano et al. [21]. The films were deposited under high vacuum conditions (10^{-6} Torr) with various (5 nm, 10 nm and 20 nm) thicknesses. Masek et al. [22] investigated the influence of preparation and annealing conditions on the physical and chemical properties of tungsten oxide thin films. The effect of annealing on the structural and optical properties of WO_3 thin films prepared by electron-beam evaporation technique were investigated by Joraid et al. [23]. However the investigations on the structural and electrical 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 structural and electrical properties of vacuum deposited WO_3 thin films were reported.

2. Experimental

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 8×10^{-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 3×10^{-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 5×10^{-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.

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 structure of WO_3 films was analysed using a Philips X-ray diffractometer with Cu K_α (λ = 1.5418 A^0) target. The X-ray diffraction profiles were recorded in the scanning angle range 10^0 - 60^0 with a scanning speed of 1 deg./ min. The dc electrical conductivity measurements were made on the experimental films by employing the standard van der Pauw method.

3. 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.

3.1 Structure

The structure of WO_3 films was analysed using a Philips X-ray diffractometer with Cu K_α (λ = 1.5418 A^0) target. The X-ray diffraction profiles were recorded in the scanning angle range 10^0 - 60^0 with a scanning speed of 1 deg./ min. The X-ray diffraction spectra of the films formed at different substrate temperatures are shown in Fig. 1. No significant diffraction peaks were observed for the films deposited at T_s < 553 K indicating the amorphous nature of films (Fig. 1(a) & 1(b)). The WO_3 films deposited at Ts ~ 503 K and subsequently annealed at 673 K for 6 hours in air showed characteristic (020), (021), (002) orientations (Fig. 1(c)) representing the orthorhombic phase of WO_3. The lattice parameters evaluated from the XRD data were 'a' = 0.728 nm, 'b' = 0.750 nm and 'c' = 0.382 nm and they are in good agreement with the reported values on WO_3 films [24-28].

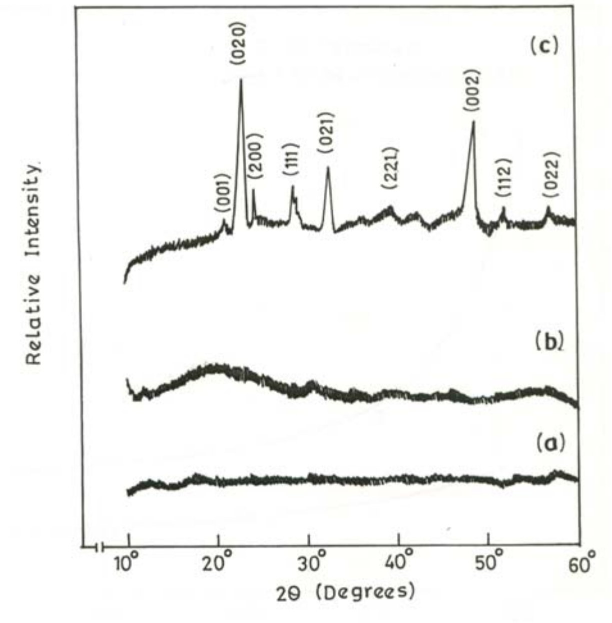

Fig.1 X-ray diffraction profiles of as-deposited and air heat treated WO_3 thin films.

3.2 Electrical properties

The dc electrical conductivity of WO_3 films formed at different substrate temperatures was measured by the four - point probe method. Fig. 2 shows the variation of electrical conductivity with substrate temperature of WO_3 films. The conductivity of the films formed at room temperature (303 K) was about 3.3 x 10^{-7} ohm^{-1} cm^{-1}. The conductivity was found to increase with increasing substrate temperature and the increase was more predominant for the films formed at $T_s > 453$ K. The increase in conductivity is mainly due to the oxygen ion vacancies formed in the films during the deposition due to the partial dissociation of constituent elements. The oxygen ion vacancies behave as positively charged structural defects in the substoichiometric WO_{3-y} films formed at elevated temperatures, where y is a small fraction [29]. The electrons may be promoted into these defects by giving electrical or optical energy thereby increasing the conductivity of the films. The WO_3 films formed at 303 – 503 K and subsequently calcinated at 673 K for six hours were found to be translucent white. The electrical conductivity of these films shown in Fig. 2 was in the range 8×10^{-8} to 4×10^{-7} ohm^{-1} cm^{-1}. The decrease in electrical conductivity of air heat treated films is attributed to partial filling up of oxygen vacancies.

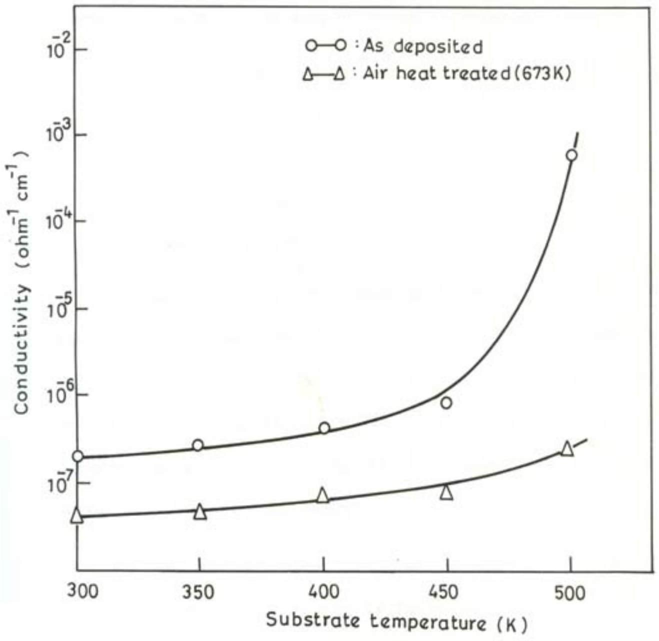

Fig.2 Dependence of electrical conductivity on deposition temperature of WO_3 thin films.

The dc conduction mechanism in many transition metal oxides above room temperature (> 303 K) takes place by band conduction, where carriers excite beyond mobility edges into non - localized states, dominating the transport. The temperature dependence of conductivity is of Arrhenius type and is expressed as

$$\sigma = \sigma_o \exp(-E_a/kT) \qquad (1)$$

σ_o, the pre — exponential factor
E_a, the thermal activation energy
k, the Boltzmann constant and
T_s, the absolute temperature.

The electrical conductivity was measured in the temperature range 303 – 503 K. Fig. 3 is a typical Arrhenius plot of log σ versus 1000/T of WO_3 films deposited at different substrate temperatures. It is observed from the figure that the conductivity increases with increasing temperature. The variation of activation energy with deposition temperature is shown in Fig. 4. The activation energy was found to decrease with increasing deposition temperature.

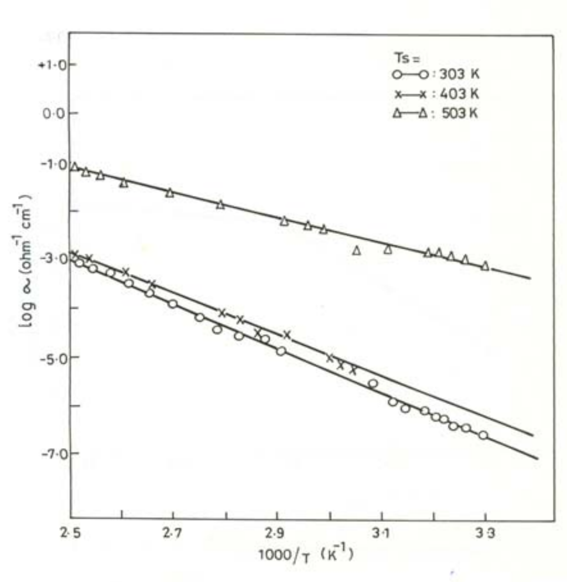

Fig.3 The plots of log σ vs $10^3/T$ of WO_3 thin films deposited at different temperatures.

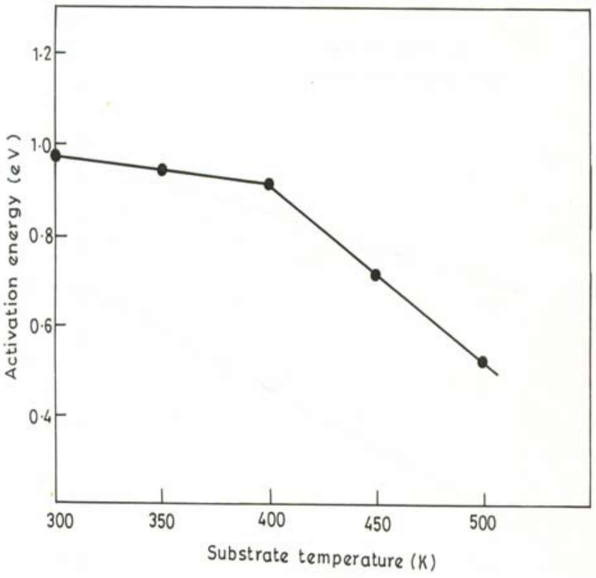

Fig.4 Dependence of activation energy on deposition temperature of WO_3 thin films.

4. Conclusion

WO_3 thin films were prepared by vacuum evaporation technique. The influence of substrate temperature on the structural and electrical properties of WO_3 films has been studied. The WO_3 films deposited at Ts ~ 503 K and subsequently annealed at 673 K for 6 hours in air showed characteristic (020), (021), (002) orientations representing the orthorhombic phase of WO_3. The conductivity was found to increase with increasing substrate temperature and the increase was more predominant for the films formed at $T_s > 453$ K. The increase in conductivity is mainly due to the oxygen ion vacancies formed in the films during the deposition due to the partial dissociation of constituent elements. The WO_3 films formed at 303 – 503 K and subsequently calcinated at 673 K for six hours were found to be translucent white. The electrical conductivity of these films was in the range 8 x 10^{-8} to 4 x 10^{-7} ohm^{-1} cm^{-1}. The substoichiometric WO_3 films formed at $T_s \sim 503$ K with high conductivity can be utilized in electrochromic devices and in solid state microbatteries.

References

[1] A.K. Arof, E.B. Saniman and M.Z. Mastor, J. Phys. III France **4**, 849 (1994).
[2] C. Julien, O.M. Hussain, L. EI Farh and M. Balkanski, Solid State Ionics **53**, 400 (1992).
[3] O.M. Hussain, A.S. Swapnasmitha, J. John and R. Pinto, Appl. Phys. A **81**, 1291 (2005).
[4] C.G. Granqvist, Solar Energy Materials and Solar Cells **60**, 201 (2000**).**
[5] P.V. Ashrit, G. Bader, V.V Truong, Thin Solid Films **320**, 324 (1998).
[6] A. Hjelm, C.G. Granqvist and K.M. Wills, Phys. Rev. B **54**, 2436 (1996**).**
[7] D. Gogova, K. Gesheva, A. Szekeres and M. Sendova-Vassileva, Phys. Stat. Sol. **176**, 969 (1999).
[8] P. Woodward and A. Sleight, J. Sol. State Chem. **131**, 9 (1997).
[9] E. Saljie and K.Viswanathan, Acta Cryst. A **31**, 356 (1975).
[10] A. Antonaia, T. Polichetti, M.L. Addonizio, S. Aprea, C. Minarini and A. Rubino Thin Solid Films **354**, 73 (1999).
[11]Y.A. Yang, J.N. Yao, J. Phys. Chem. Solids **61**, 647 (2000).
[12] R. Sivakumar, R. Gopalakrishnan, M. Jayachandran and C. Sanjeeviraja, Smart Mater. Struct. **15**, 877 (2006).
[13] S. Papaefthimiou, G. Leftheriotis and P. Yianoulis, Solid State Ionics **139**, 135 (2001).
[14] L. Meda, R.C. Breitkopt, T.E. Haas and R. U. Kirss, Thin Solid Films **402**, 126 (2002).
[15] P. Tagtstrom and U. Jansson, Thin Solid Films **352**, 107 (1999).
[16] A. Monteiro, M.F. Costa, B. Almeida, V. Teixeira, J. Gago and E. Roman, Vacuum **64**, 287 (2002).
[17] S.C. Moulzolf, L.J. Le Gore, R.J. Lad, Thin Solid Films **400**, 56 (2001).
[18] N. Sharma, M. Deepa, S.A. Agnihotry, Solid State Ionics **152**, 873 (2002).
[19] O.M. Hussain, A.S. Swapnasmitha, J. John and R. Pinto, Appl. Phys. A **81**, 1291 (2005).
[20] G. Soto, W. De La Cruz, J.A. Diaz, R. Machorro, F.F. Castillon and M.H. Farias, Appl. Surf. Sci. **218**, 281 (2003).
[21] L. Ottaviano, M. Rossi and S. Santucci, Thin Solid Films **490**, 59 (2005).
[22] K. Masek, J. Libra, T.S. Kala, M. Cabala, V. Matolin, V. Chab and K.C. Prince, Surf. Sci. **600**, 1624 (2006).
[23] A.A. Joraid and S.N. Alamri, Physica B **391**, 199 (2007).
[24] S.K. Deb, Philos. Mag. **27**, 801 (1973).
[25] S.S. Sun and P.H. Holloway, J. Vac. Sci. Technol **A2**, 336 (1984).
[26] H. Kaneko, F. Nagao and K. Miyake, J. Appl. Phys. **63**, 2 (1988).
[27] Z. Guanghui, S. A. Wessel and K. Colbow, J. Phys. D: Appl. Phys. **21**, 1802 (1988).
[28] A. Donnadieu, D. Davazoglou and A. Abdellaovi, Thin Solid Films **164**, 333 (1988).
[29] G. Hollinger, T.M. Due and A. Deneuville, Phys. Rev. Lett. **37**, 1564 (1976).