CHAPTER-IV

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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF SPRAYED WO₃ THIN FILMS

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STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF SPRAYED TUNGSTEN OXIDE THIN FILMS

4.1 INTRODUCTION :

In the last two decades several investigations have been the [1-5] performed both on electrochromic and photoelectrochemical [6,7,10,11] properties of WO₃ .These properties of the films depend largely on their structure [17] which inturn depend on the method: of preparation of the films. The WO₂ thin films have been prepared by several methods such as thermal evaporation [1], sputtering [12,13], reactive sputtering [14,15] and anodic oxidation of metallic tungsten [10]. However, very few reports are available on the preparation of WO_3 thin films by spraying solutions onto the hot substrates [11,16].

This chapter presents, effect of concentration of spraying solution on different properties of tungsten oxide thin films. The concentration of the spraying solution was varied from 0.01 M to 0.05 M and the films were studied for their structural, optical and electrical properties. The tungsten oxide films deposited on amorphous glass substrates were used for these characterizations.

4.2 EXPERIMENTAL :

4.2.1 THICKNESS MEASUREMENTS

Film thickness is an important parameter in the study of the film properties. Amongst different methods for measuring the film thickness, the weight difference method is simple and convenient and thickness 't' is measured using the relation,

$$t = \frac{m}{A \cdot \rho} \qquad \dots \qquad (4.1)$$

where, 'm' is the mass of the film deposited on area 'A' of the substrate and $\rho_B^{}$ is the density of the material in the bulk.

4.2.2 SURFACE MORPHOLOGY :

Surface morphology of the WO₃ thin films has been examined by using following two techniques :

a) Transmission optical microscopy :

Surface morphology of the tungsten oxide films has been observed from optical micrographs taken with the help of transmission microscope, Leitz Wefzlar (Germany), Type 307. This gives an indication of uniformity of the thin films.

b) Scanning electron microscopy :

Surface morphology of the films has been observed from SE micrographs taken with the help of Scanning Electron Microscope, Cambridge Stereoscan 250, MK-3 unit. This helps to study the microstructure of the surface and to findout the grain size of the thin film.

4.2.3 X-RAY DIFFRACTION :

X-ray diffraction technique is useful tool for structural investigations [28,29]. Philips PW 1710 X-ray diffractometer, using CuK_{α} radiation with wavelengths (α_1 , α_2):1.54060 A^O, 1.54438 A^O was used. The X-ray tube was operated on 25kV,20 mA.

The XRD patterns for the films were recorded within the span of angles 20 to 80° .

4.2.4 IR TRANSMISSION SPECTROSCOPY :

IR transmission spectra were obtained with the help of IR spectrophotometer, Perkin-Elmer 783 unit.

4.2.5 OPTICAL ABSORPTION SPECTROSCOPY :

The films prepared were analysed by the optical absorption studies. The variation of optical' absorption density 'a t' with wavelength ' λ ' for the films was carried out, in 350 to 850 the wavelength range nm, with the spectrophotometer, Hitachi 330. This data were further analysed for the estimation of the bandgap energy.

4.2.6 ELECTRICAL RESISTIVITY :

Resistivity ' ρ ' measurement methods cover the entire range of contact and non-contact approaches and studied by various authors [22-27]. In this study, the two point probe technique has been adopted to study the resistivity of tungsten oxide films.

A brass block was used as a sample holder-cum-heater. The area of the film was defined and silver paste was applied to ensure good electrical contacts to the films. Chromel-Alumel thermocouple was used to measure the mean temperature. The resistivity of the film was studied in the temperature range 300 to 475 K.

4.3 RESULTS AND DISSCUSSION :

4.3.1 THICKNESS MEASUREMENTS :

Thickness of the films prepared at different solution concentration was calculated by weight difference method. Fig.4.1 shows the variation of film thickness with concentration of sprayed solution. It is observed that the thickness increases almost linearly with the concentration.

4.3.2 SURFACE MORPHOLOGY :

a) Transmission Optical Microscopy :

Fig.4.2(a,b,c) shows the transmission optical micrographs with X 250 magnification; of films prepared with solutions of different concentrations. It is observed that all the films are uniform and pin hole free.

b) Scanning Electron Microscopy :

The scanning electron micrograph of a typical film with X 3000 magnification is shown in Fig.4.3. The close examination of the SEM reveals the well defined grain structure of the film. Conttrell's method [18] is used to calculate the grain size of the WO_3 thin film. This method relates the number of intercepts of grain boundary per unit length of a reference circule and is given by,

$$P_{L} = (\frac{n}{2 \pi r}) M \dots (4.2)$$

where 'n' is the total number of intercepts, 'r' is radius of $^{r_{e}}$ ference circle and 'M' is magnification. Using P_L, the grainsize 'L' can be determined as,



Fig.4.1 : Variation of film thickness with concentration of sprayed solution







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$$L = \frac{1}{P_L - 1}$$
(4.3)

The grain-size of the film calculated by using above method is $\simeq 0.4~\mu\text{m}$.

4.3.3 X-RAY DIFFRACTION :

Fig.4.4(a,b,c,d,e) shows the XRD patterns of the films prepared at different concentrations. The well^c defined (distinct) peaks observed in the XRD patterns indicates that the films are polycrystalline in nature.

Table 4.1 (a,b,c,d,e) shows the comparison of the experimental data with the ASTM data. From the comparison it is found that the films consists of mixed tricline and monoclinic structures of tungsten oxide with some minor peaks corresponding to d-values of oxygen deficient tungsten oxide compositions. Also it is observed that the peaks corresponding to oxygen deficient tungsten oxides increases with increase in concentration of solution indicating that the composition is more oxygen deficient as the concentration of the solution increases. Similar XRD results are reported by others [1,2,4,10].

4.3.4 IR TRANSMISSION SPECTROSCOPY :

The IR transmission spectra of the films mere found to be similar to that of the standard IR spectra of WO_3 [21], except an additional peak at wavenumber 720. This peak may be related to the traces of WO_4^{-2} ions in the film. The standard IR spectra and that of a typical film spectra is shown in Fig.4.5.



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Fig.4.4 (a,b,c,d,e) : XRD patterns of the films deposited with (a) 0.01 M(b) 0.02 M (c) 0.03 M (d) 0.04M and e(e) 0.05 M solutions

-•- For triclinic WO₃ peaks and -X - for monoclinic W_{25} O₇₃ peaks

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Peak angle	Observed I/I 'd' values		Possible identification with standard		
(2 🖯)	% max		triclinic WO ₃	Monoclini	c W ₂₅ O ₇₃
1	2	3	4	5	
a) 0.01 M S	Solution				
21.78	76	4.08	-	4.17 (10)14)
22.88	100	3.88	3.84 (002)	-	
25.82	16	3.45	-	3.48 (30)6) 👻
26.76	16	3.33	3.34 (021)	. –	
28.44	14	3.14	3.14 (112)	-	
28.96	24	3.08	3.08 (112)	-	
29.66	32	3.01	-	2.99 (1112)
30.58	15	2.92	-	-	
33.08	18	2.71	2.71 (022)	-	
33.90	22	2.64	2.64 (220)	-	
b) 0.02 M	Solution				
21.85	38	4.06	-	4.17 (10	014)
23.12	49	3.84	3.84 (002)		
23.64	63	3.76	3.76 (020)	_	
24.35	100	3.65	3.65 (200)	-	
26.64	12	3.34	3.34 (021)	-	
28.17	36	3.16	3.14 (112)		
28.75	15	3.10	3.08 (112)	۰ ــــــــــــــــــــــــــــــــــــ	
32.98	23	2.71	2.71 (022)		
33.32	21	2.69	2.67 (202)		
34.17	40	2.62	2.63 (202)	-	
36.85	14	2.44	-	-	
49.92	25	1.83	-	1.88 (60)6)
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Table**41** Comparison of observed XRD data for different films with ASTM data

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<u> </u>	2	3	4	5		
c) 0.03 M	Solution					
21.53	100	4.12	-	4.17	(1014)	
23.24	2.5	3.82	3.84 (002)	3.82	(010)	
23.96	2	3.71	3.76 (020)	- ،		
25.17	3	3.53	-	-		
32.70	50	2.74	2.71 (022)	-		
56.14	11	1.64	-	1.68	(325)	
d) 0.04 M Solution						
23.04	39	3.86	3.84 (002)	, –	-	
24.50	100	3.63	3.65 (200)	-		
25.88	24	3.44	-	-		
28.94	13	3.08	3.08 (112)	-		
29.78	13	3.00	-	2.99	(1112)	
34.16	34	2.62	2.62 (202)	-		
35.74	16	2.51	$2.52(\bar{2}21)$	-		
50.60	9	1.80	-	1.87	(5016)	
55.86	9	1.65	-	1.68	(325)	
e)0.05 M Solution						
21.62	84	4.11	-	4.17	(1014)	
22.93	26	3.88	3.84 (002)	-		
23.45	35	3.79	3.76 (020)	-		
24.16	37	3.68	3.65 (200)	-		
32.77	100	2.73	_	2.71	(4012)	
33.09	18	2.70	2.71(202)	-		
34.00	24	2.63	2.63 (202)	-		
49.75	13	1.83	-	1.87	(5016)	
56.21	49	1.64	-	1.68	(325)	
68.90	23	1.36	-	-		

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4.3.5 OPTICAL ABSORPTION MEASUREMENTS :

Fig.4.6 shows the optical absorption spectrographs for films prepared with different concentrations. The analysis of the plots shows that comparatively thinner (t < 1 μ m) films didnot show clear absorption edge while the others (t < 1 μ m) showed a steep absorption edge in the observed range of photon energies.

The optical bandgaps of the material were determined by plotting graphs of $(\alpha \ h\nu)^2$ versus h_V and are shown in Fig.4.7.

The values of the bandgaps of the films prepared with solution concentrations 0.03, 0.04 and 0.05 M were 2.62, 2.54 and 2.42 eV respectively; decreasing with increase in concentration of the sprayed solution. Eventhough many workers have reported that tungsten oxide is indirect band gap material (4-9); the plots of $(\alpha h\nu)^2$ versus $h\nu$ show clear absorption edge; indicating that the material is direct band gap. Similar results are reported by Deb [1] and Koffyberg et al [19].

4.3.6 ELECTRICAL RESISTIVITY :

Fig.4.8 shows the variation of electrical resistivity at room temperature (27 ° C) with the concentration of sprayed solution. The resistivity of films decreases with increase in concentration of sprayed solution as shown in the figure. A remarkable drop in electrical resistivity is observed for films



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Fig.4.6 : Variation of room temperature electrical resistivity with concentration of sprayed solution.

prepared with concentration higher than 0.02 M (t > 1 μ m).The temperature dependence of electrical resistivity of the films was measured in the range 300 to 475 K and is shown in Fig.4.9. The nature of the graph indicates semiconducting nature of the films.These plots for films with thickness above 1 μ m are almost linear while a kink is observed at about 375 K for films with thickness less than 1 μ m indicating the presence of a critical thickness below which electrical properties of films change considerably. Table 4.2 shows variation of electrical resistivity at room temperature and thermal activation energies of the films prepared with solutions of different concentrations.

Table 4.2 : Variation of electrical resistivity at room temperature and thermal activation energies of the films prepared with solutions of different concentrations

Conc.of solution used M	Film thickness µm	Electrical resistivity at 27 ⁰ C ohm-cm	Thermal activation energy eV		
0.01	0.28	4.25×10^{6}	Low temp.range 0.072		
		:	High temp.range 0.260		
0.02	0.44	2.58 × 10 ⁶	Low temp.range 0.040		
		-	High temp.range 0.260		
0.03	1.02	7.01 X 10 ³	0.075		
0.04	1.62	7.17 \times 10 ²	0.067		
0.05	2.21	4.16 \times 10 ²	0.056		



Fig.4.9 : Temperature dependance of the electrical resistivity of films deposited with different solution concentrations.

From the table it is found that, there is no systematic variation of activation energies with the concentrations of the sprayed solutions. The activation energies in all the cases may be originated due to the presence of defect levels and are analogous with the energy of self trapping of carriers. Miyake et al [8] reported the activation energies in the range 0.06 to 0.1 eV for reactively sputtered tungsten oxide films.

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- [1] S.K.Deb, Phil.Mag., 27 (1973) 801.
- [2] Konstanty Marszalek, Thin Solid Films 168 (1989)133.
- [3] F.G.K.Baucke, Solar energy. Mater., 16 (1987)67.
- [4] K.Miyake, H.Kaneko, M.Sano and N.Suedomi, J.Appl.Phys.,
 55 (7) (1984) 2747.
- [5] K.Miyake, H.Kaneko, N.Suedomi and S.Nishimoto, J.Appl.Phy., 54(9) (1983) 5256.
- [6] Francesco Di Quarto, Guiseppe Russo, Carmelo Sunseri and Agatino Di Paola, J. Electrochem. Soc. Far. Trans. I -78 (1982) 3433.
- [7] M.A.Butler, J.ApplPhy., 48(5)(1977)1914.
- [8] K.Miyake, H.Kaneko and Y.Teramoto, J.Appl.Phy., 53(3)(1982) 1511.
- [9] Martine Spichinger-Ulmann and Jan Augustynski, J.Appl.Phy., 54(10) (1983) 6061.
- [10] Benjamin Reichman and Allen J.Bard, J.Electrochem.Soc., 126(12) (1979)2133.
- [11] Gary Hodes, David Cahen and Joost Manassen, Nature, 260(1976) 312.
- [12] G.G.Barna, J.Electron.Mater.,8(1979)153.
- [13] E.K.Sichel and J.I.Gittleman, J.Electron Mater.8(1979)1.
- [14] H.Kaneko, K.Miyake and Y.Teramoto, J.Appl.Phy.53(1982) 4416.
- [15] H.Kaneko, K.Miyake and Y.Teramoto, J.Appl. Phy., 53(1982) 3070.

- [17] J.P.Randin and R.Viennet, J.Electrochem.Soc., 129(1982) 2349.
- [18] A. Contrell, An introduction to metallurgy (Arnold, London, 1975) P-173.
- [19] F.P.Koffyberg and F.A.Benko Appl.Phy.lett.37(1980)320.
- [20] S.H.Pawar, P.S.Patil and C.D.Lokhande Ind.J.Pure and Appl.Phys.New Delhi, 27(1989)227.
- [21] R.A.Nyquist and R.O.Kagel "Infrared spectra of Inorganic compounds" Academic Press, New York and London (1971).
- [22] I.R.Weingarten and M.Rothberg, J.Electrochem.Soc., 108 (1961) 167.
- [23] T.O.Poehler and W.Liben, Proc.IEEE 52(1964)731.
- [24] J.Lepage, A.Bernalte and D.A.Linholm, Rev.Sci.Instrum. 39(1968) 1019.
- [25] S.C.Choo and E.L.Heasell, Rev.Sci.Instrum, 33(1963)1331.
- [26] J.N.Bhar, Proc.IEEE 51 (1963)1623.
- [27] V.K.Subashiev, Sov.Phys.Solid State, 5(1963)405.
- [28] H.Hahn,G.Frank,W.Kingler,A.Meyer and C.Storger Z.ANORG Chem.271 (1953)153.
- [29] D.R.Crow, 'Principles and Applications of Electrochemistry ', Chapman and Hall, London (1974).