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Short Communication

Growth and Characterization of Vacuum Evaporated WO_3 Thin Films for Electrochromic Device Application

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Abstract

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 composition and structure of WO_3 films has been studied. The density of the films was found to be dependent on the substrate temperature and increased from 5.0 to 6.5 g/cm (accuracy ± 0.1 g/cm^3) with increasing temperature from 303 to 553 K and then slightly decreased with further increase of temperature. The films formed at Ts ~ 503 K and heat treated in air at 673 K for six hours showed 20.59 wt% of oxygen indicating that the films attained highest oxidations state (W^{+6}) which is comparable with the starting material. 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.

Key words: WO_3 thin films, vacuum evaporation, density, composition, structure.

Introduction

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 form using various deposition techniques and finds their effective use in scientific and technological applications. 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].

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. 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 growth and characterization 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 compositional analysis was carried out by LINK AN - 10000 EDAX analyser attached to the JEOL JSM - 6400 Scanning electron microscope. The structure of WO_3 films was analyzed 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.

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.

Density: WO_3 films formed at Ts < 403K were found to be translucent white. The colour of the films changed to pale blue and then to deep blue with increasing deposition temperature. The apparent density of the films was estimated using the measured values of film thickness, area and weight of the oxide film (using sensitive micro - balance having an accuracy of ± 1 g). The calculated density of the tungsten oxide films with deposition temperature is shown in figure-1. The density of the films was found to be dependent on the substrate temperature and increased from 5**.0** to 6.5 g/cm (accuracy ± 0.1 g/cm^3) with increasing temperature from 303 to 553 K and then slightly decreased with further increase of temperature.

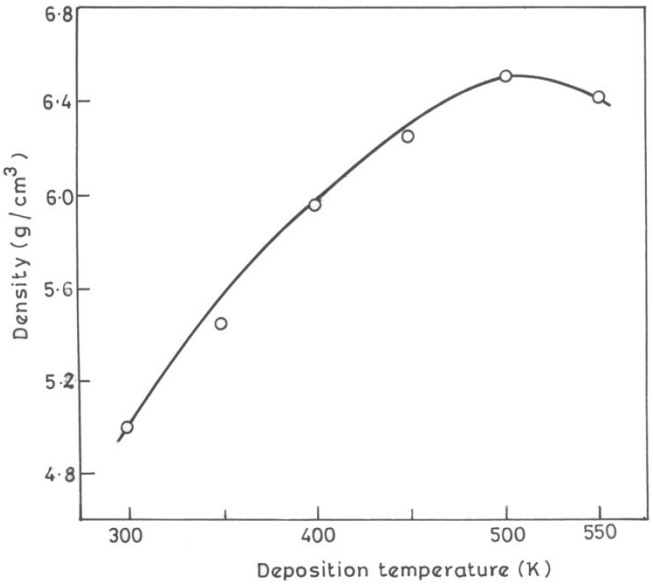

Figure-1
Dependence of density on deposition temperature of WO_3 thin films

Composition: The compositional analysis was carried out by LINK AN - 10000 EDAX analyzer attached to the JEOL JSM - 6400 Scanning electron microscope. The weight percentage of the constituent elements in WO_3 films formed at different substrate temperatures is given in **table-1.** The content of tungsten and oxygen in WO_3 source powder are 79.30 wt% and 20.70 wt% respectively. The wt% of tungsten and oxygen in the WO_3 films formed at room temperature were found to be 79.5l wt% and 20.48 wt% respectively indicating that the films were nearly stoichiometric. The oxygen content decreased with increasing substrate temperature and it was 19.84 wt% in the films deposited at 503 K due to partial dissociation. This indicates that the films formed at elevated temperature are substoichiometric $WO_{3-y,}$

where y is a small fraction. The films formed at Ts ~ 503 K and heat treated in air at 673 K for six hours showed 20.59 wt% of oxygen indicating that the films attained highest oxidations state (W^{+6}) which is comparable with the starting material.

Table - 1
Composition Analysis of Tungsten Oxide Thin Films

	Weight percentage (wt %)	
Sample	**Tungsten**	**Oxygen**
WO_3 Powder	79.30%	20.70%
WO_3 film (Ts~ 303K)	79.51%	20.48%
WO_3 film (Ts~ 503K)	80.16%	19.84%
WO_3 film (Ts~ 503K) and Calcinated at 673K	79.40%	20.59%

Structure: The structure of WO_3 films was analyzed 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 figure-2[10]. No significant diffraction peaks were observed for the films deposited at T_s < 553 K indicating the amorphous nature of films (Fig. 2(a) & 2(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. 2(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[11,12].

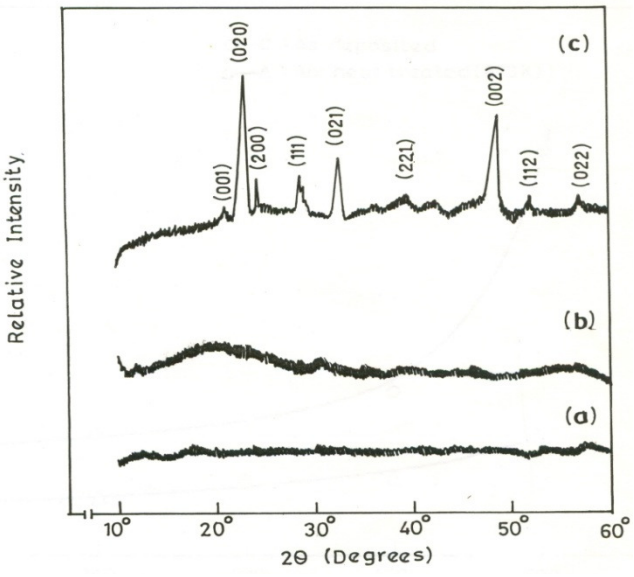

Figure-2
X-ray diffraction profiles of as-deposited and air heat treated WO_3 thin films.

Dc Electrical Conductivity: 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

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

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

The variation of the dc conductivity of air heat treated film (films formed at T_s ~ 503 K) was studied and is shown in figure-3. The activation energy of the heat treated films was found to be 0.88 eV which was found to be in good agreement with the data obtained by Kaneko et al.[13].

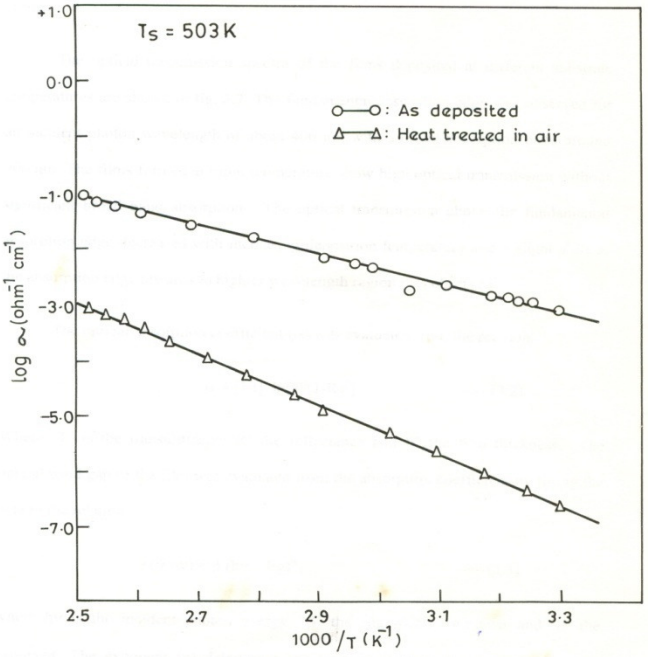

Figure-3
The plots of log σ vs 10^3/T of as-deposited and air heat treated WO_3 thin films.

Conclusion

WO_3 thin films were prepared by vacuum evaporation technique. The influence of substrate temperature on the composition and structural properties of WO_3 films has been studied. The density of the films was found to be dependent on the substrate temperature and increased from 5**.0** to 6.5 g/cm (accuracy ± 0.1 g/cm^3) with increasing temperature from 303 to 553 K and then slightly decreased with further increase of temperature. The films formed at Ts ~ 503 K and heat treated in air at 673 K for six hours showed 20.59 wt% of oxygen indicating that the films attained highest

oxidations state (W^{+6}) which is comparable with the starting material. 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. These substoichiometric WO_3 films can be utilized in electromic devices and in solid state microbatteries.

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