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Growth, microstructure and electrochromic properties of activated reactive evaporated WO_3 thin films on flexible substrates

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The tungsten trioxide (WO_3) thin films were deposited onto flexible ITO coated Kapton substrates using plasma assisted activated reactive evaporation technique. The film depositions were carried out at an optimized glow power and oxygen partial pressures of 8 W and 1 X 10^{-3} Torr respectively. The WO_3 thin films deposited at a substrate temperature of 473 K were found to be composed of uniformly distributed nano grains with a triclinic structure. These nano crystalline WO_3 thin films showed 73% optical transmittance in the visible region with an optical band gap of 3.34 eV. The film exhibited an optical modulation of 53 % upon lithium insertion and estimated coloration efficiency at a wavelength 550 nm is about 45 cm^2/C.

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1. Introduction

In the modern science and technology era, thin films of transition metal oxides (TMOs) are of great interest and opened windows for innovative challenges in diverse fields for future advanced technologies [1]. The electrochromic technology is one of the demanding fields, which triggered the designing and fabrication of efficient electrochromic devices (ECDs) with an immense potentiality such as advanced smart windows [2]. These ECDs work on the phenomenon of electrochromism, in which a reversible optical modulation in the materials can be accomplished by intercalation/deintercalation of small cations (Li^+) and electrons by the application of small electric filed. Among various electrochromic (EC) transition metal oxides, tungsten trioxide (WO_3) in thin film configuration is recognized as one of the best alternative and extensively investigated EC material, because it exhibits large optical modulation, good durability, low power consumption and less stress for viewer's eyes [3]. Several physical and chemical vapor thin film deposition techniques have been adapted to deposit tungsten trioxide thin films onto ITO coated glass substrates and have been meticulously studied their electrochromic properties [4, 5]. But the electrochromic properties of tungsten trioxide films primarily depend on their microstructural properties such as crystallinity, structure, stoichiometry, binding energy, porosity in the films and density of the films, which in turn depend upon the type of thin film deposition technique [6]. Plasma deposition methods are growing world wide acceptance for the deposition of refractory compounds such as carbides, nitrides, sulfides, oxides and related materials. Activated reactive evaporation (ARE) is one of the plasma deposition techniques with high deposition rate. The main advantages of activated reactive evaporation process are three folds [7]: (i) the reaction occurs predominantly in plasma, (ii) the chemical composition of the film can be controlled by changing the ratio of reacting species and (iii) high melting point inorganic compounds can be synthesized at lower substrate temperatures.

The deposition of tungsten trioxide thin films onto the flexible substrates and their use as active layers in advanced smart windows to enhance their indoor and out door compliance with persistent electrochromic properties, is the currently challenging and dynamic objective for the researchers. Therefore there is an adequate necessity to grow electrochromic thin film active layers onto flexible substrates from the fabrication of flexible smart window technology point of view. To the best of our knowledge, very few researchers have reported the electrochromic properties of tungsten trioxide thin films deposited onto flexible substrates. Toshiaki et. al [8] have prepared tungsten trioxide thin films on flexible ITO coated substrate by PLD technique and observed the colour change from transparent to blue after the applied DC voltage and A. Azens et. al [9] adapted electrochromic coated flexible foils and investigated their optical and cyclic voltammetric properties. Considering the significance of flexible smart windows based WO_3 thin films, the investigations were carried out carried out to grow tungsten trioxide thin films on ITO coated Kapton substrate using plasma assisted activated reactive evaporation technique. The microstructure, optical and electrochromic properties of thin films were studied.

2. Experimental

Thin films of tungsten trioxide were deposited using home built activated reactive evaporation (ARE) technique [10]. The substrates were Kapton sheets coated with ITO thin films prepared by sputtering at room temperature, in the experimental set up that has been already described [11]. The ARE system contains two circular electrodes of equal cross sectional area, separated by the distance of 4 cm. The strong and uniform magnetic field is provided between the two electrodes to achieve high density of plasma. A dc power supply with a current rating of 1 A at 2000 V was used as the power source. The deposition chamber initially evacuated to a base pressure of 5×10^{-6} Torr and high purity oxygen was allowed as the reacting gas and its flow was controlled by using Tylon mass controller. High density of plasma was established between the source and substrate by allowing the pure oxygen between two circular electrodes and by applying high dc voltage across the two electrodes. The characteristics of obtained plasma were investigated by studying the current-voltage (CV) characteristics of the glow discharge as shown Fig. 1. From the experimental observations, it is noticed that the strength of plasma is observed to improve with the enhancement of glow power and with the augmentation of oxygen partial pressure in the deposition chamber. The degree of ionization of the gas gives the density of the charge particles in the plasma and it specifies the fractions of the particles in the gaseous phase, which are ionized. The degree of ionization increases by the increase of glow power and oxygen partial pressures. From the C-V characteristics of the glow power, high density and stabilized glow can be achieved at high glow power and oxygen partial pressure as shown in the Fig. 1. Hence in the presentation all the tungsten trioxide thin film deposition were carried out at an optimized glow power and oxygen partial pressures of 8 W and 1×10^{-3} Torr respectively by maintaining an ambient substrate temperature of 473 K.

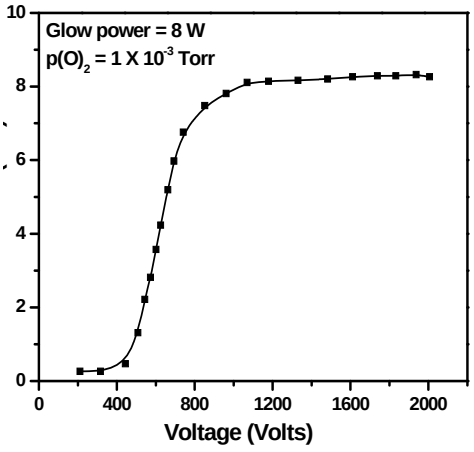

Fig. 1. Current-Voltage characteristics Glow discharge

The structurural characteristics of the as deposited WO_3 thin films were investigated using Grazing incidence X-ray diffraction (GIXRD) technique (Siefert computerized X-ray diffractometer, model 3003 TT) with a grazing incidence of angle 3^0. Atomic force microscopy (AFM) (Digital instruments, Dimension 3100 series) was used to study the surface morphology of the films in a simple contact mode of separation. The compositional studies of the WO_3 thin films were explored by the method of X-ray photoelectron spectroscopy (XPS) by using an ISA Riber Mac 2 electron spectrometer with Mg K_α radiation (1253.6 eV). The binding energy was calibrated with reference to the C (1s) level of carbon (285 eV). The Raman spectroscopic studies were performed on WO_3 thin films using the Raman-laser apparatus (Jobin – Yvon U1000) to understand the crystal system in the films in the wave number range 200 – 1200 cm^{-1}. The optical measurements were carried out by Hitachi U-4300 UV-VIS-NIR double beam spectrometer in the wavelength range of 300 – 1500 nm. Lithium insertion studies were investigated by a dry method in which lithium niobate ($LiNbO_3$) was heat-treated under high vacuum to give off lithium atoms for insertion in the exposed WO_3 films. The degree of such lithiation was measured by noting the charge in the quartz crystal thickness (the effective mass) and calibrated against the electrochemical insertion [12].

3. Results and discussion

The GIXRD pattern of tungsten trioxide films grown at substrate temperature of less than 473 K exhibited diffused diffraction profiles by indicating the amorphous nature of the films. For the films deposited at substrate temperature greater than or equal to 473 K, the respective diffraction pattern displayed pronounced and broad characteristic envelop in the 2θ range $23 - 25^0$ in the films as shown in Fig. 2. The characteristic Bragg reflections (002), (020) and (200) were indexed at respective diffraction angles and the average lattice constants evaluated from the GIXRD data are a = 7.311 Å, b = 7.521 Å and c = 7.677 Å, attributed to the triclinic structure, which are in good agreement with the JCPDS data (Card No. 20-1324) and also with the data reported for PLD tungsten trioxide thin films by K.J. Lethy et al. [13]. The estimated crystallite size using Scherrer's formula is found to be in the order of 60 nm. From the above, it is clear that the onset of crystallinity starts at lower substrate temperature of 473 K. This is because, in activated reactive evaporation technique, the intense ion-species bombardments in presence of plasma lead to the greater energy and momentum transfer with each other and associated to the increase of their kinetic energy. This process provides sufficient energy for the adatoms on the surface and augmentation of crystallinity in the films at lower substrate temperatures.

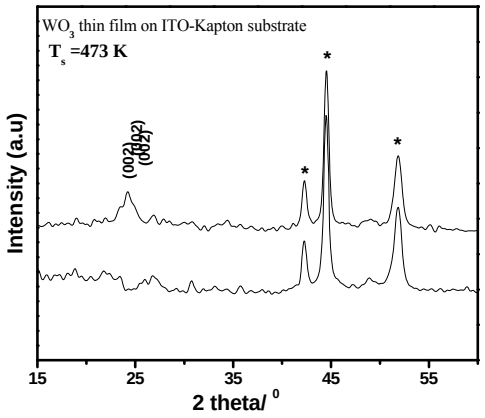

Fig. 2. The X-ray diffractograms of WO_3 thin films grown onto ITO coated flexible substrate at T_s = 473 K.

The XPS spectra of the films exhibited the core level binding peaks corresponding to W $4f_{7/2}$ and W $4f_{5/2}$ peaks at 35.5 eV and 37.6 eV respective binding energies with spin-orbit separation of 2.1 eV, which indicates the presence of tungsten at W^{6+} state [14]. The surface morphological characteristics of activated reactive evaporated tungsten trioxide thin films at substrate temperature of 473 K have been studied by AFM as shown in the fig. 3. The AFM image data demonstrated the activated reactive evaporated tungsten trioxide thin films were found to be homogeneous and uniform with regard to the surface topography. The AFM morphological data reveal that the film is composed of nano clusters with vertical cone like projection of varying sizes provided by large internal volume with an average grain size of about 68 nm and root mean square surface roughness of about 8 nm. The obtained AFM data is in agreement with the GIXRD data of the film.

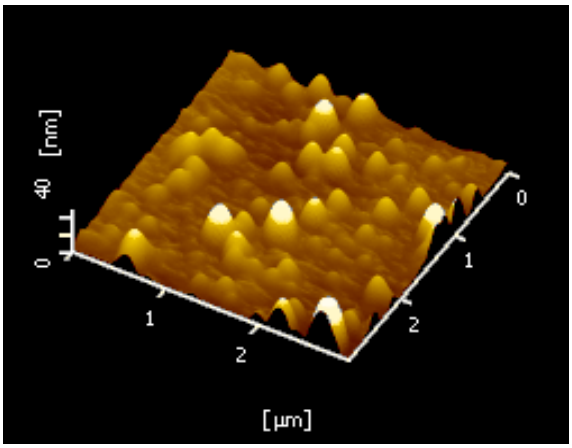

Fig. 3. The AFM picture of tungsten trioxide thin film grown onto ITO coated flexible substrate.

The Raman spectra is recorded for the tungsten trioxide thin film grown onto ITO coated flexible substrate as represented in the fig. 4. The Raman bands were indexed at 716 cm^{-1} and 807 cm^{-1} were attributed to symmetric stretching and asymmetric stretching vibrations of O-W-O and bands assigned at 278 cm^{-1} and 334 cm^{-1} were attributed to the bending vibration of δ(O-W-O). The bands pointing at 807, 716 and 278 cm^{-1} is distinctive in either monoclinic or triclinic phase [15]. The longer bonds are the source of the 716 cm^{-1} peak, while the shorter O-W-O bonds are responsibles for the stretching mode at 807 cm^{-1}. The broad feature at 950 cm^{-1} observed for films deposited at substrate temperature of 473 K can be assigned to W^{6+} = O stretching mode of terminal oxygen atoms present on the surface of clusters and micro-void structures in the film [16]. The RS band at 950 cm^{-1} is also attributed to W = O stretching modes at grain boundaries which become observable when the grain size is in nano meter range [17]. The nano structured tungsten trioxide films are usually thought to be composed of O-W-O units and WO_6 octahedra of the bulk crystal with terminal W = O bonds on their boundaries.

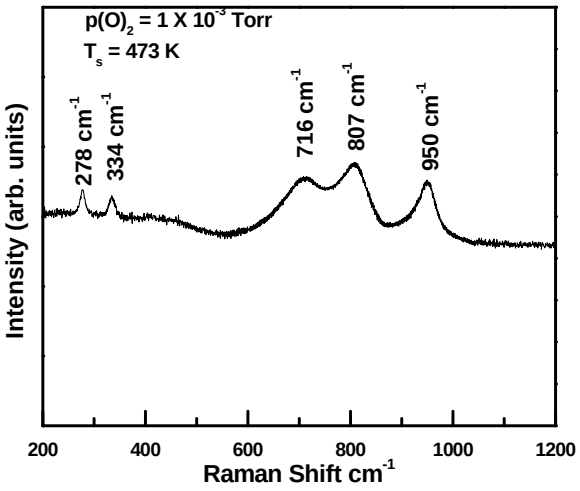

Fig. 4. The Raman spectrum of tungsten trioxide thin film onto flexible substrate.

The optical transmittance spectrum was recorded in the wavelength range 300 – 1500 nm for tungsten trioxide thin films deposited at substrate temperature of 473 K as represented in the Fig. 5. The as deposited film exhibited nearly 73% of optical transmittance in the visible region. The optical absorption coefficient (α) is evaluated from the optical transmittance and reflectance data [18]. The experimentally measured optical absorption coefficient for tungsten trioxide films is found to give better fit for n = ½ indicating direct band gap. The optical band gap was estimated by extrapolating the linear region of the plot to zero absorption and noticed that as deposited nano crystalline tungsten trioxide films prepared onto ITO coated flexible Kapton substrate possessed an optical band gap of 3.34 eV as shown in the Fig. 5a. This estimated band gap value is slightly higher than that of the optical band gap of crystalline WO_3 (3.24 eV). The fundamental

absorption edge in tungsten trioxide thin films is mainly due to inter valence transitions from 2p valence band of oxygen to the 5d conduction bands of tungsten. In the optical transmittance spectra of nano crystalline tungsten trioxide films grown at lower substrate temperatures, a slight shift in the absorption edge is observed towards the lower wavelength, in comparative with conventional crystalline films. This blue shift in the nano-crystalline tungsten trioxide thin films with lower grain size may be due to the quantum confinement of the clusters and existence of small grain boundaries and imperfections, which lead to the larger free carrier concentration and the existence of potential boundaries. The electric fields arising from these factors in the nano crystalline tungsten trioxide thin film may responsible for consisting of higher band gap at lower substrate temperature. The refractive index of the film was estimated at the wavelength of 550 nm and found to be 1.76 and the estimated relative density of the film using Lorenz - Lorenz relation was 0.65 [19].

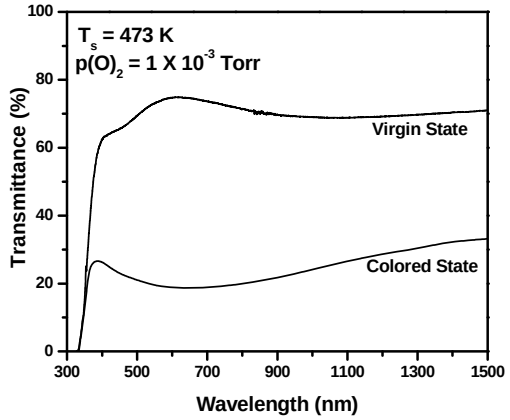

Fig. 5. The optical transmittance spectra of tungsten trioxide thin films in both virgin and colored states.

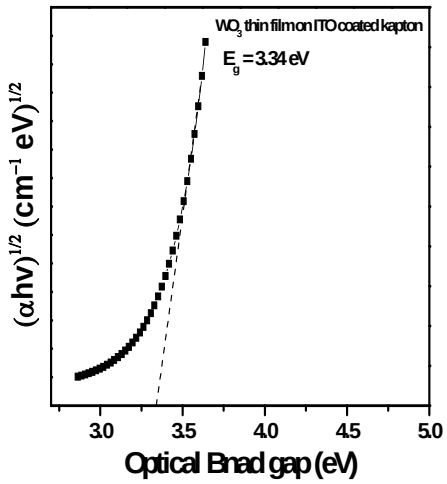

Fig. 5a. The plot of $(\alpha h\nu)^{\frac{1}{2}}$ vs. $h\nu$ for tungsten trioxide thin film grown at T_s = 473 K.

The electrochromic studies were carried out for the tungsten trioxide thin films deposited on ITO coated Kapton substrate using dry lithiation method as reported by P.V. Ashrit et al. [20]. The $LiNbO_3$ powder was heat treated in vacuum to expel lithium atoms which are inserted into tungsten trioxide thin films kept at temperature of 373 K, to give coloration for the films and the variation of the optical transmittance of tungsten trioxide thin films in colored state as shown in the Fig. 5. When lithium atoms reach the exposed tungsten trioxide thin film surface they diffuse into the films and affect the thickness of the films. The measured thickness of the film using quartz crystal monitor and the quantity of the lithium intercalated into the film are measured by monitoring the frequency change of the quartz crystal as the mass of tungsten trioxide and lithium are deposited. The maximum coloration studied here is for 20 nm effective mass thickness of lithium which corresponds to approximately 12.5 mC/cm^2 as demonstrated from the electrochromical method. It is observed that nano crystalline tungsten trioxide thin films deposited on ITO coated flexible Kapton substrate exhibited a reasonably good optical modulation of 53 % in colored state in the visible region. The estimated coloration efficiency at a wavelength of about 550 nm is about 45 cm^2/C. Though our results are lower than the reported values of the sputtered WO_3 thin films coated on transparent conducting glass substrates by A. Subrahmanyam et al. [21] the obtained results in the present investigation are encouraging and useful in flexible smart window applications. Further investigations are in progress to study the electrochromical properties of the films using cyclic voltammetry.

4. Conclusions

Nano-crystalline tungsten trioxide thin films were successfully deposited on ITO coated flexible Kapton substrate maintained at 473 K using plasma assisted activated reactive evaporation technique. The films exhibited triclinic structure with an average crystallite size of about 60 nm. In the visible region the films exhibited an optical transmittance of 73 % with an evaluated band gap of 3.34 eV. These films demonstrated a reasonably good coloration efficiency of 45 cm^2/C at the wavelength of 550 nm.

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