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Studies on Electron Beam Evaporated WO₃ Thin Films

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Abstract

Among Transition metal oxides, tungsten trioxide (WO₃) is one of the most interesting electrochromic materials, which can be colored through electro-, photo- and thermo chromic processes. The interesting physical properties of these films allow practical applications such as energy saving windows, anti glare rear view mirrors and multicolor electrochromic devices. In this view of tremendous applications, WO₃ thin films were deposited by electron beam evaporation technique onto well cleaned glass, Indium Tin Oxide (ITO) coated glass substrates and Si wafer at different substrate temperatures. The present work reports on the influence of the substrate temperature on the optical and structural properties. The crystallization of WO₃ thin films starts, as we are raising the substrate temperature. Atomic Force Microscopy (AFM) measurements have been carried out in order to understand the growth mechanism.

Keywords: Tungsten trioxide, Electron beam evaporation, AFM, FT-IR Optical Properties.

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1. Introduction

Transition metal oxides (TMO) represent an interesting class of materials possessing a wide variety of properties due to the unique nature of outermost d-electrons present. They have layered type of structure, either two
dimensional vanderwaal’s bonded layer structure or three dimensional frame work tunnel structure [1,2]. The stoichiometric deviations in these TMOs may be due to anion or cation deficiency. The combination of these materials with thin film technology reduces the size of the device significantly which leads to the miniaturization and micro electronic technology.

Among these transition metal oxides, tungsten trioxide (WO₃) is a wide bandgap n-type semiconductor, has been extensively studied material due to its interesting physical and chemical properties which make them useful in catalysts, electrochromic devices, gas sensors, sun roofs, smart windows, rear view mirrors [3-7]. 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 and shows structural transformations and sub-stoichiometric phase transitions [9].

Now a days, there is a considerable interest in the development of devices that can be used for optical switching which is based on electro-, photo- and thermo-chromism process. The transmittance of WO₃ films can be changed in a reversible manner by the intercalation/deintercalation of small cations and electrons into the film. The major function of electrochromic windows is to control the flow of light and heat passing through them [8,9]. Upto now, the electrochromic devices not reached the technical levels in the direction of reliability, stability and low cost production. The electrochromic properties like coloration efficiency, cyclic durability depend on the structural, morphological and optical properties and hence on the deposition parameters and deposition techniques. So far a large number of deposition techniques have been developed to prepare thin films of WO₃ [10-13]. Out of those techniques, electron beam evaporation technique has been chosen for present studies, in which the contamination probability is least and high deposition rates can be achieved. By keeping the above facts in view, our investigations are aimed at deposition of WO₃ thin films by electron beam evaporation technique at different deposition parameters and the study of structural, vibrational and optical properties of the above deposited films

2. Experimental Technique

WO₃ thin films were prepared by using electron beam evaporation technique (3KW EBG POWER SUPPLY, V.R. Technology, Bangalore). Pure WO₃ (99.99%) powder obtained from Sigma Aldrich Co were taken in required proportion and made into pellets of 1cm diameter and 0.15cm thickness. These pellets are calcinated at about 1073K for 7 hours. The films were deposited onto either rectangular, optically flat glass substrate (from MICO) which are chemically, ultrasonically and glow discharge cleaned or Si wafer and also on Indium Tin Oxide (ITO- from Sigma Aldrich Co) coated substrates. The source to substrate distance was fixed at 14 cm. The films were prepared at different substrate temperatures RT, 250, 350 and 450°C and in the vacuum 2x10⁻⁵ mbar. The thickness of the films and the deposition rate were controlled by quartz crystal thickness monitor and found to be 200 nm and 0.2 nm/sec respectively. The WO₃ in the pellet form, taken in a graphite crucible and kept in water cooled copper hearth of electron gun. The pelletized WO₃ targets were heated by means of an electron beam collimated from the d.c heated tungsten filament cathode. When the electron beam can be bent into 270⁰ and bended beam is incident on the pelletized WO₃ target, the surface was bombarded with electron beam with an accelerating voltage of 5KV and a power density of about 3K W/cm². In this process the evaporation is taken place in a high vacuum to allow molecules to move freely in a chamber and hence condense on all surfaces including the substrate. The surface structure of the deposited films was determined by NT-MDT Solvernext Atomic Force Microscope (AFM). The infrared transmittance of the films was recorded in the wavenumber range 600-1200 cm⁻¹ using a Shimadzu FTIR Spectrophotometer (IR Prestage-21). The optical properties were studied by recording the transmission spectra using Shimadzu UV 1800 spectrophotometer in the wavelength range 300-1100 nm. The optical bandgap values were calculated.
3. Results and Discussion

3.1 AFM Studies

The surface morphology of grown WO₃ thin films were studied by using AFM. The morphological features like grain size, shape, surface roughness are dependent on growth process and deposition parameters. Fig. 1 shows the three dimension (3D) atomic force micrograph images of WO₃ thin films deposited at different substrate temperatures. The images clearly showed that grain size varies with substrate temperature. The films deposited at room temperature (Fig.1 (a)) are having uniform smooth surfaces which show the amorphous nature of the films. The figure shows individual columnar grains sticking out from the surface with average grain size of about 40 nm and surface roughness of about 1.5 nm. As the substrate temperature raised from room temperature, the surface roughness of the films was found to be increased from 2.2 to 3.5 nm dramatically and also the grain size increases slightly, due to the agglomeration of grains together to form larger ones of size about 70 nm to 82 nm (Fig.1(b)&(c)). Further increase in the substrate temperature made the grain boundaries become more visible. The structure became relatively discrete and found some valleys. Even though the particle size is increased, the bumps of the particles are decreased [10]. As the substrate temperature increases, the mobility of atom on the surface also increases which leads the formation of larger grains [11].

![AFM Images](image1)

Fig.1. AFM images of the surface of WO₃ thin films grown at substrate temperature (Tₛ): (a) RT, (b) 250°C, (c) 350°C and (d) 450°C.

3.2. FT-IR Studies

The Vibrational studies of WO₃ thin films were studied by recording FT-IR spectra in the transmittance mode in the wave number range from 600-1200 cm⁻¹ which is shown in Fig.2. The spectra reveal broad absorption band which shows the presence of stretching modes of W-O in the films deposited at room temperature. As the films were deposited at substrate temperatures the broad band splits into two lines at 718 and 802 cm⁻¹ corresponding to w-o stretching vibrations in the crystalline monoclinic WO₃[12]. At high temperatures the peak at 629 cm⁻¹ clearly
shows the disordered framework structure. The broad bands above 1000 cm\(^{-1}\), belongs to Si-O bonds due to Si substrate. The strong absorption in the 600–900 cm\(^{-1}\) region is assigned to the W–O vibrations such as in WO\(_3\) [13]. The absorption peaks above 1000 cm\(^{-1}\) were not clear and the main bands are below 1000 cm\(^{-1}\) which shows the crystallization [14].

![FTIR Spectra of WO3 thin films grown at substrate temperature (T_s): (a) RT, (b) 250°C, (c) 350°C and (d) 450°C.](image)

3.3. Optical properties

The wavelength dependence of optical transmittance for the deposited WO\(_3\) thin films onto glass and ITO coated glass substrates were shown in fig (3 (a) and (b)). A relative high transmission of the films shows that the films are weakly absorbing and the sharp decrease in the transmission at about the wavelength 350 nm corresponds to the fundamental absorption edge. As the substrate temperature increases reduction in the transmittance was clearly observed due to the oxygen deficiency, and also due to the higher carrier concentrations which absorbs light. It is also clearly observed that the transmittance of WO\(_3\) thin films deposited on ITO coated glass substrate has shown significant reduction, even though the films were deposited at same deposition parameters. This dimension can be attributed to varying wetting effects of two surfaces and difference in the morphologies of the substrates with raising of temperature. The optical absorption coefficient (\(\alpha\)) which gives the relative rate of decrease in light intensity can be determined from the above data by using the relation [10]

\[
\alpha = -\ln[T]/t
\]

Where ‘T’ is the transmittance and ‘t’ is the thickness of the films.

The Optical energy band gap of these films were determined from the transmission spectra using Tauc’s relation [10], given as

\[
(\alpha h\nu) = \beta (h\nu - E_g)^n
\]

Where \(h\nu\) is the incident photon energy, \(\beta\) is the edge width parameter and \(n\) is the exponent. The exponent \(n\) depends on the type of optical transitions in the material and can take the values 1/2, 3/2, 2 and 3 for transition being direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively [15]. The optical data for the above deposited films gave a better fit for the exponent \(n=2\) representing the indirect allowed transitions [9, 10].
Fig. 4 show the plots of \((\alpha h\nu)^{1/2}\) versus \(h\nu\). It is clearly observed from the graphs that the band gap values are decreasing with increase of substrate temperature from 3.158 to 3.067 eV on glass substrates and from 3.249 to 2.93 eV on ITO coated glass substrates. The optical data also supports the crystallization in WO₃ thin films as the temperature raises and more specifically on ITO substrates [16].

4. Conclusion

The influence of substrate temperature on morphological, vibrational and optical properties of Tungsten trioxide thin films prepared by electron beam evaporation technique deposited at different substrate temperatures were studied in the present investigation. The surface roughness and the grain size of the films varies dramatically with increase of the substrate temperature from room temperature. The Vibrational studies shows broad absorption band at room temperature and with increase in the substrate temperature it shows clearly the stretching vibrations at 718 and 802 cm\(^{-1}\) in the crystalline monoclinic WO₃. The optical absorption data had given a better fit for the exponent \(n=2\), suggesting the indirect allowed transitions with band gap ranging from 3.158 to 3.067 eV on glass.
substrate and from 3.249 to 2.93 eV on ITO coated glass substrates with respect to the substrate temperature. It is also found that the optical band gap values decreases with increasing substrate temperature. The decrement in the band gap value at higher substrate temperatures supports the crystalline structure.

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