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Tunsten Oxide Thin Films by Reactive Sputtering Gas Pressure Ratios

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Abstract: Tungsten trioxide (WO_3) is a highly industrial important electrochromic compound. It was prepared onto ILFORD glass substrate by reactive RF sputtering technique. Films were deposited at different gas pressure ratios of Ar:O_2 [1:2, 1:3,1:4,1:5] in order to the energy regimes of the sputtered particles on the condensing surface. The electrical conductivity is also studied by using four-probe method. Electrical measurement shows that resistivity of films is found to decrease with increase of film thickness. The carrier concentration and mobility is also calculated by Hall Effect measurement. It proves the WO_3 is an n-type semiconductor.

Keywords : Tungsten oxide, RF sputtering technique, Argon and oxygen**.**

1. Introduction

Initially Scientists showed their interest only in bulk material. Then their concentration was turned on thin films. A bulk material is said to be in thin film form when it is built up as a thin layer on a solid support called substrate by controlled condensation of the individual atomic molecular or acetone ionic species either directly by a physical process or via chemical or electrochemical reaction [1].In this present work an attempt has been made to characterize the WO_3 film on ILFORD glass substrate. The ILFORD glass plates are well cleaned by acetone solution and clean with the dry cotton. Now the plates are ready for sputtering technique. Tungsten oxide (WO_3) compound became a subject of intensive studies due to its novel electrochromic properties such as optical, gas sensing, electrochormatic etc [1]. Thin films have been finding wide applications in various fields like solar energy convertors, radiation detectors, highly reflective mirror coating[1] microelectronics-electrical conductors, electrical barriers, diffusion barriers, magnetic sensor, gas sensors, SAW devices, optics-anti reflection coating, corrosion protection, wear resistance, electronic-layers of insulators, semiconductors and conductors for integrated circuits [1].Thin films devices for windows, mirrors, rechargeable Li-ion batteries and space application have become an essential part of modern technology[2].Among electrochromic materials, WO_3 is the most well studied. It has potential for in smart windows which allow dynamic control of the solar energy converters. Many variations of these basic vapour deposition methods have been developed in efforts to balance advantages and disadvantages of various strategies based on the requirements of film purity, structural quality and the rate of growth, temperature constraints and other factors. The crystal structure has been studied by high resolution microscopy and extends defects characterized by crystallographic shear planes, pentagonal and bipyramidal columns and hexagonal and pentagonal cross-sections. The structural properties of WO_3 film is studies using x-ray diffraction technique. Optical studies are also carried out using UV-Vis-NIR spectrophotometer (Hitachi-3400) .Electrical properties are also carried out using the four probe measurement.

In sputter deposition, ions of a sputtering gas, typically Ar, are accelerated toward the target at high speed by a imposed electric field. The initial concentration of charge carrier in the system is significantly increased with an increase in the dc voltage, as the ions collide with the cathode, thereby releasing secondary electrons and with the neutral gas atoms. As critical numbers of electrons and ions are created through such avalanches, the gas begins to glow and the discharge becomes self-sustaining. Gaseous ions striking the target or the source material from which the film is made dislodge surface atoms which form the vapor in the chamber. The target is referred to as the cathode since it is connected to the negative side of the direct current power supply. The chamber is evacuated and the Ar gas, at a pressure of ~13.3 pa (10^{-1}torr), is introduced for the purpose of maintaining a visible glow discharge. The Ar^+ ions bombard the target or cathode, and the ensuing momentum transfer causes the neutral atoms of the target source to be dislodged. These atoms transit through the discharge and condense onto the substrate thus providing film growth.

In sputtering the bombardment of the target source by Ar^+ ions imparts a high kinetic energy to the expelled source atoms. Although sputter deposition promotes high surface diffusivity of arriving atoms, it also leads to greater deflects nucleation and damage the deposition surface because of the high energy of the atoms, while it is not well studied for epitaxial growth of films .For polycrystalline films, the film grain structure resulting from sputter deposition typically has many crystallographic orientations without preferred texture, sputter deposition offers better control in maintaining stoichiometry and film thickness uniformity than evaporative deposition and has the flexibility to deposit essentially any crystalline and amorphous materials.

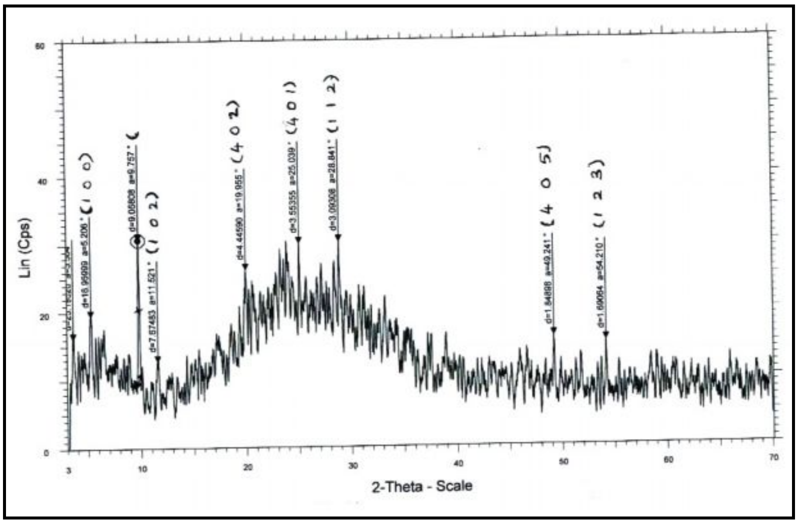
2. Experimental Procedure

Tungsten oxide films were prepared by sputtering technique using a HIND HIVAC vacuum coating with RF power supply. The degreased substrates were mounted on the substrate holder and placed into the coating chamber. Tungsten target of about 2 inch diameter is used. Now the chamber was closed and evacuated using the rotary and diffusion pumps. After achieving the required vacuum high vacuum of order $2x10^{-6}$ m bar with sputtering pressure $2x10^{-2}$m bar the process gets started. By applying the constant pressure of Argon and oxygen inside the chamber it gets readily react with the target material. The resultant was obtained with a RF power of 200W. The ablated material (w) target with the inlet of pressure and power it was evaporated and the evaporated vapour phase condensed and deposited as thin film on the substrate as WO_3.The distance of the substrate from the target material is about 5.5cm. The observed films were uniform, pin hole free, well adherent to the substrate and transparent in nature. The depositions were carried out at different $Ar:O_2$ ratios via 1:2,1:3,1:4,1:5 at room temperature(RT).The room temperature prepared films were further annealed at 100,150 and 200C for 2 hrs in the presence of oxygen environments.

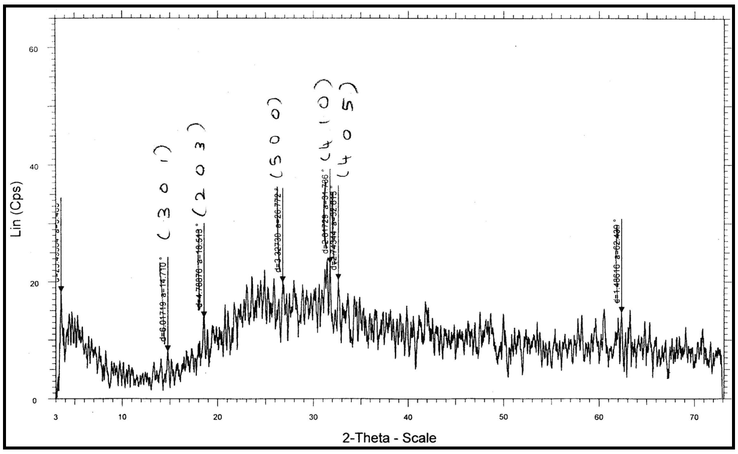
3. Results and Discussions

3.1 Structural Studies

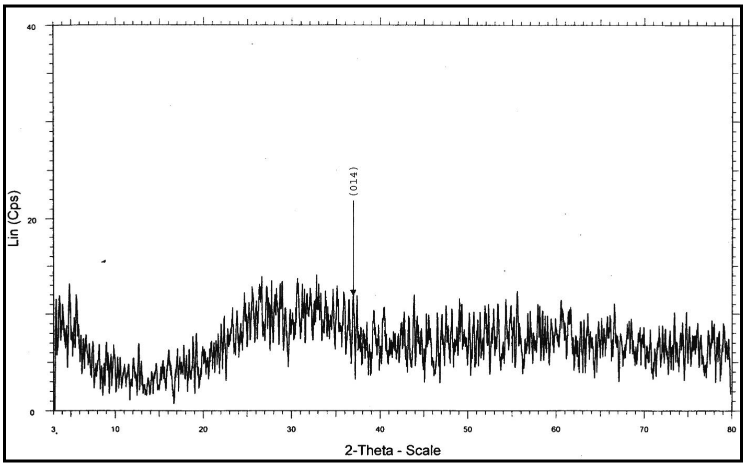
The structural characteristics of the prepared WO_3 thin films have been studied using an X-ray diffractometer Bruker AXS D8 Advance with a nickel filtered Cu-Kα radiation (λ=1.54A) at 40KV and 30mA. The thickness of the depostited films has been determined using stylus method. The X-ray diffractogram of the as-deposited films of WO_3 compound of 1:2 RT are shown in Fig.1



1:3RT



1:4RT



1:5RT

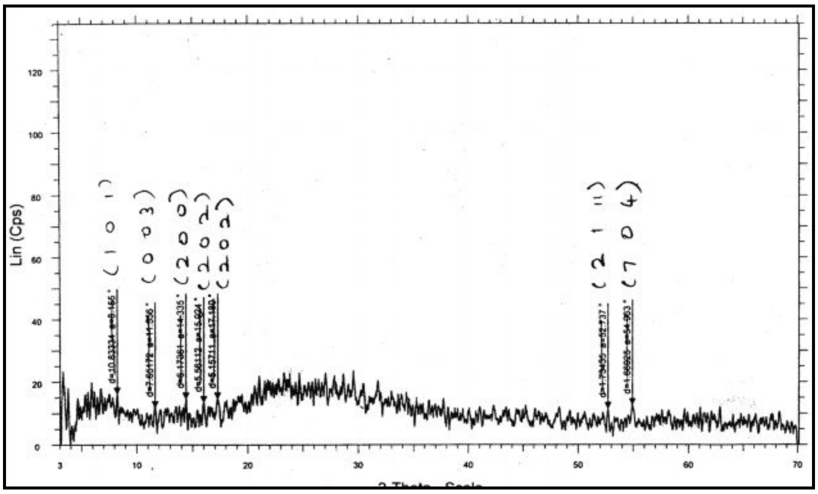


Fig.1. The X-ray diffraction spectra of WO_3 thin films were prepared by reactive sputtering method with different ratios 1:2,1:3,1:4,1:5 on glass substrates

The sample 1:3 and 1:4 show less deominant peaks but the sample at Ar:O_2 presssure ration 1:2 and 1:5 show prominent peaks showing the tungsen oxide formation in the films.The X-ray diffraction spectra of WO_3 thin films were prepared by reactive sputtering method with different ratios 1:2,1:3,1:4,1:5 on glass substrates are shown in Fig.1. The obsverved interplanar distance of the films are compared with the standard JCPDS data[73-2177,65-5468,73-2177,73-2182] for as-deposited films. It is concluded that the optimized films in the present study belong to the monoclinic [3,4] crytal system. The peak heights may be improved on heat treatment of the film at higher temperatures [5]. So, the samples annealed at 200°C shows good results,. The annealed sample of Ar:O_2 pressure ration 1:2 at 473K for 2 hours shows the presence of diffraction peaks corresponding to tungsten ixide in the (101) plane orientation. The annealed sample WO_3 is also monoclinic [3,4] in structure .The XRD spectra of these WO_3 compound is shown in the fig XRD spectrum of tungsten oxide (1:2) at 473K. Least square refinement technique was used for the estimation of cell parameters. The lattice parameter values a,b,c and β have been determined for the sample A and are found as 16.959,3.433 and 17.293A92.8 respectively. Similarly good results are obtained for the sample D as 12.354,3.749 and 22.969A, 92.0 respectively. These results are found to be in good agreeement with the results of earlier workers[6].

3.2 Electrical Studies: Resistivity measurements

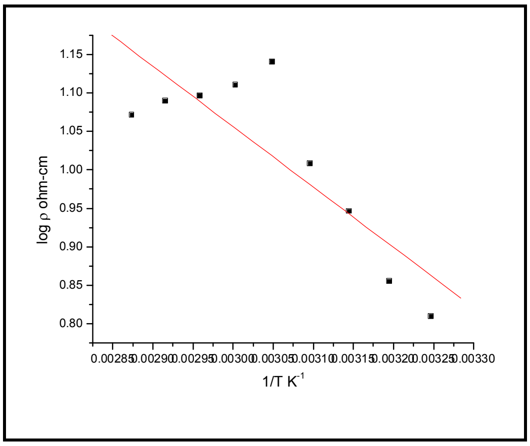
Four probe techniques are used to find the resistivity measurements. The resistance of WO_3 film deposited on glass substrates varies with temperature (Room temperature to 473K).The resistance is found to decrease with increase in the temperature which confirms the semiconducting nature of WO_3 films. The resistance of the films is found to decrease with increase in film thickness. This may be due to the presence of large grains with less strain and less dislocations in the thicker films. Table shows the variation of resistivity and activation energy for samples A, B, C, D. The resistivity is found to vary for different samples and different thickness of the deposited films. The activation energy of the deposited WO_3 films (Room temperature to 473K) have been calculated from the log p versus 1/T plots as shown in the Figs 2 & 3. The activation energy values obtained are shown in the Table.1.

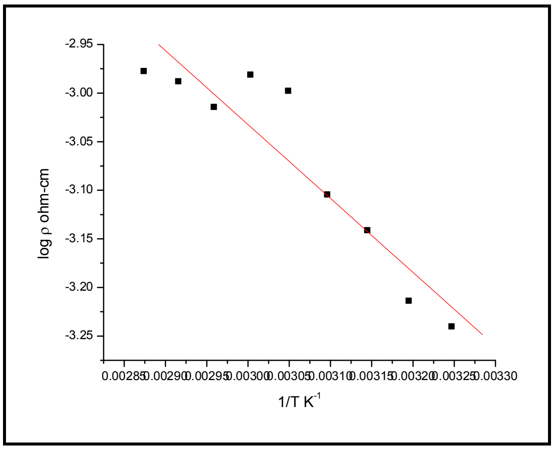
Table.1 shows the variation of resistivity and activation energy for samples A, B, C, D

WO_3 at different ratios	Thickness µm	Activation Energy E_a (eV)	Resistivity (ρ) Ohm – cm
1:2	0.13	0.0675	2.55×10^3
1:3	0.15	0.0655	5.6314
1.4	0.18	0.0297	4.6067
1.5	0.32	0.0325	$.203 \times 10^3$

3.2.1 Variation of activation energy and resistivity with film thickness

From the Arrhenious plot, we know that the conductivity increase with increasing temperature.





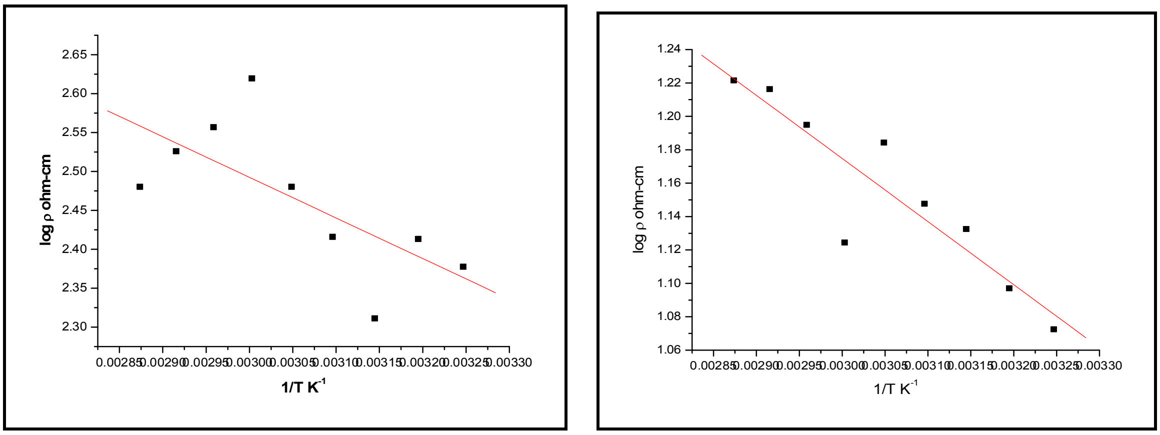


Fig.2 Plot of log ρ vs 1/T of WO_3 thin film deposited at Room Tempterature

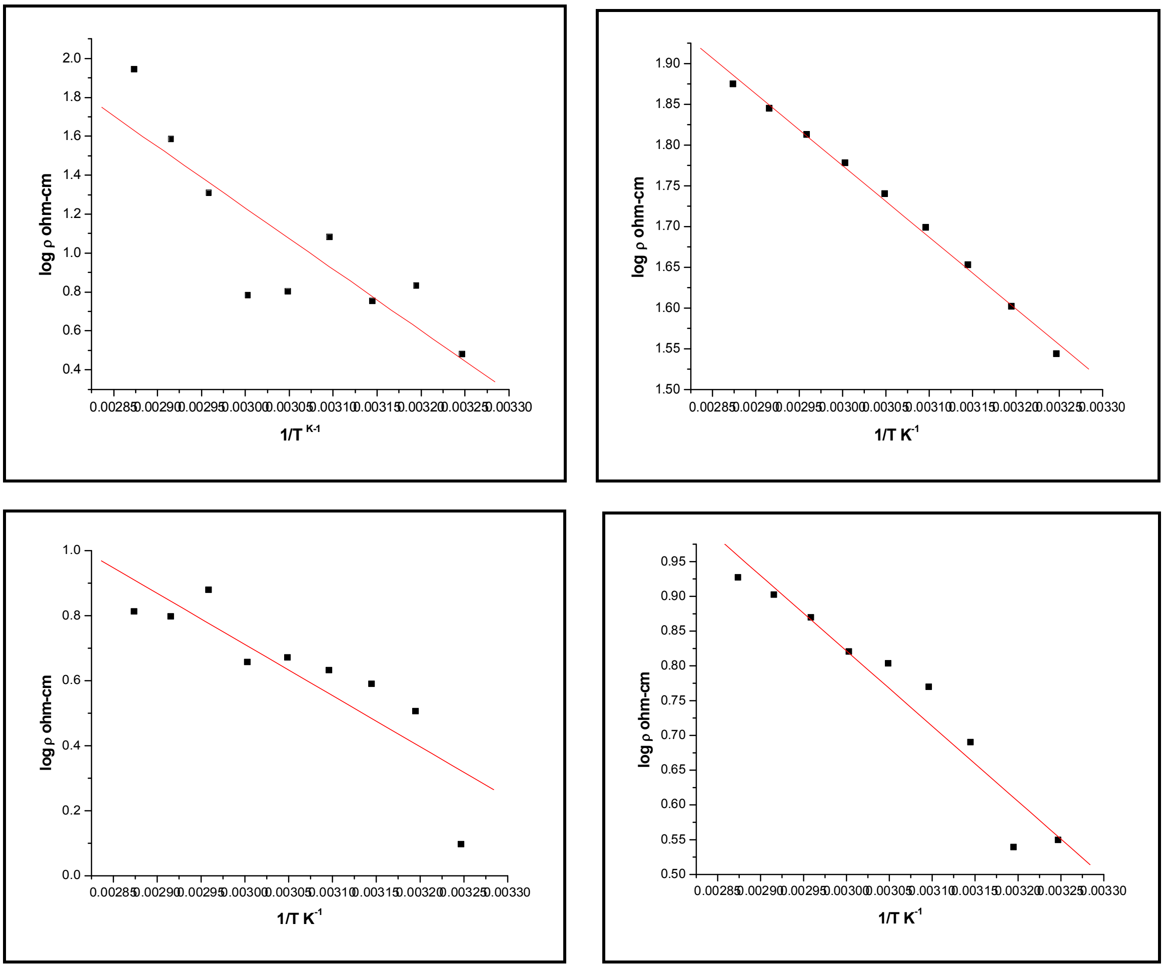


Fig.3. Plot of log ρ vs 1/T of WO_3 thin film annealed at 473 K

3.3 Hall Effect Measurement

The Hall Effect studies have been carried out on WO_3 thin films deposited on glass substrates at room temperature. From the Hall Effect studies it has been observed that WO_3 thin films are of n-type semiconductor. This agrees with the reports available so far. From the measurement carrier concentration, the Hall coefficient and Hall mobility are determined. The carrier concentrations of the film depend upon the band gap of the sample. The Hall mobility is highly structure sensitive and depends on nature, size and shape of the defects. The Hall coefficient (Rh) is found to be $1.1370x10^{-3}$ Ωm/Tesla. The Hall mobility (μ) is 0.0055x10-3cm^2/V-sec. The carrier concentration (n) is analysed as $9.1829x10^{21}cm^{-3}$. From the Van der Pauw technique when the magnetic fields are switch off, the Hall set up is used for resistivity measurements.

3.3. 1 Hot probe technique

From the hot probe method, the conductivity of WO_3 film can be identified. This method concludes that WO_3 is an n-type semiconductor [7] (i.e)., the current flows from cold junction to hot junction. This obeys the principle of Seeback effect. The samples of WO_3 at different ratios with current are given in Table.2.

Table.2 Current measurements on Hot probe technique

WO_3 films at different ratios	Current (mA) at RT	Current (mA) at 473K
1:2 RT	-0.9	-1.1
1:3 RT	-1.2	-0.6
1:4 RT	-1.6	-0.2
1:5 RT	-0.7	-1.0

For the samples A and D the current increases for annealed samples than as-deposited samples, whereas the samples B and C the as-deposited films increase in current than annealed samples.

3.4 Fourier Transform Infrared Spectrophotometer (FT-IR)

The FTIR spectrum was recorded using ~EXUS 670 FTIR spectrometer with FT-80 Horizontal grazing angle accessory. The spectrum was recorded in the wave number range 400-4000cm^{-1} and can be divided into two regions based on the internal and external modes .The internal modes can be described in terms of stretching and bending of W-O bonds. Generally they correspond to absorption bands in the high-frequency region. The external modes normally lie in the low frequency region and can be represented as relative motions of structural units with respect to each other i.e,translation and vibrations. The FTIR transmittance spectrum revealed information about the phase composition as well as the way oxygen is bound to be metal ion (M-O) structures. The IR transmittance spectra of the annealed WO_3 thin film at 473K for 2 hours using the reactive sputtering technique in the wavelength range 400-4000cm^{-1} is shown in Fig.4.

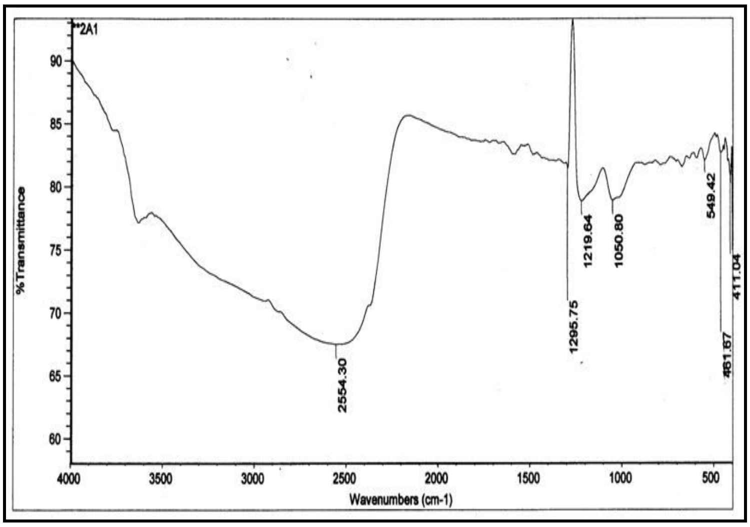


Fig.4 FTIR spectrum of WO_3 thin film

Fourier Transform IR spectra were recorded for the WO_3 thin film annealed at 200 C (sample A). The peak position of the model is an indication for the structural quality of samples. The absorption peak position of the mode along with the others IR active modes are used to evaluate the structural quality of the films. Usually the peaks observed between the wavelength range 3550cm^{-1} and 3900cm^{-1} in oxide films were assigned the OH-O stretching of hydrogen bonded hydroxyl molecules. In the presence case the spectrum manifested that the broad band appearing at 2554.30cm^{-1} of the annealed 200C sample A is a clear evidence for the presence of weakly hydrogen bonded hydroxide ions(due to the v-OH modes).Thus the presence of water molecules can be identified due to the presence of their bending vibrations.

Also, the broad small peaks between 1295cm^{-1} and 1050cm^{-1} are assigned to the deformation band in water and to the C-O stretching absorption in bicarbonate and carbonate ions. Ultimately the peak at 1219cm^{-1} is assigned to the deformation band in water. Further the band at 1050cm^{-1} may be assigned to the C-O stretching absorption in the carbonate and bicarbonate ions. There impurities most likely due to the exposure of the films and humid atmosphere. From these observations it is well known that H_2O and CO_2 molecules are chemisorbed on to the grown WO_3 surfaces. Therefore, a small amount of impurity was likely incorporated in the film during preparation and exposure to atmosphere.

The appearance of the three string band 549cm^{-1}[8] 461cm^{-1} and 411cm^{-1} in the FTIR spectrum is a clear evidence for the presence of the crystalline WO_3. The intense absorption at 549cm^{-1} observed in the spectra of the film is due to the v(W-O-W) stretch mode. These absorbance bands are the finger print bands for the confirmation of oxide films. Thus it is evidenced from the above observations that the film consist mostly of WO_3 with a small concentration of hydration. Even though there are impuries in the films, the percentage of contamination is very small. The FTIR spectra reveal the spectrum of WO_3 thin films. The IR active stretching modes are recorded at 1295 and 1050cm^{-1}.

4. Conclusion

Electrochromic WO_3 thin film is successfully deposited on (ILFORD Glass plates, England) substrate and glass substrate under optimized condition through reactive sputtering technique. The films are in uniform coating on the substrates. The films are well adherent on the substrate pinholes free, uniform and thick. From the preliminary colour observation, the films are confirmed as WO_3 films. Films prepared under optimized conditions are characterized by X-ray diffraction. X-ray diffraction shows that the films are crystalline, stoichiometric and monoclinic structure of WO_3 thin films. The films annealed at 200°C in the ratio 1:2 also show the monoclinic structure. Prepared film are polycrystalline and the preferential orientation is along the (101) plane. Oxide phase formation is identified with the FTIR spectrum. The metal-oxide bonds in the finger-print region (549 to 411cm^{-1}) confirm the WO_3 phase formations. Electrical measurement shows that the resistivity of the films is found to decrease with increase of film thickness. This is due to the presence of large grains with less strain and dislocations in thicker films. From the electrical measurements, the activation energy, resistivity, and conductivity are calculated. Hall Effect measurements prove that WO_3 is an n-type semiconductor. The carrier concentration, the Hall mobility and the Hall coefficient mainly depends on the bandgap of the sample. From the hot probe technique, the current flows from cold junction to the hot junction, proves that WO_3 is an n-type semiconductor. One can extend this problem for electro chromic devices. Smart window materials are in the thrust area in recent years.

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