CHAPTER -VII

SUMMARY AND CONCLUSIONS

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Tungsten oxide in the form of thin films is an interesting material to study. The reason for this interest are numerous. The semiconducting and photoelectrochemical properties of the thin films depend largely on their structure which in turn depend on the method of preparation of the films. WO_3 thin films have been prepared by various physical and chemical techniques. However, few reports are available on the preparation of WO_3 thin films by spray pyrolysis technique. Good stability in aqueous electrolytes is the most significant property of the material which attracts a researcher to study the photoelectrochemical properties of the thin films. Tungsten oxides, unlike tungsten chalcogenides, are less studied mateials specifically for its use as a photoanode in photoelectrochemical cells.

In this investigation, an attempt has been made to prepare WO_3 thin films by thermal decomposition of sprayed ammonium tungstate solution on to glass, F.T.O. coated glass substrates. All preparative parameters like substrate temperature, spray rate, concentration of spraying solution have been optimized. The structural, optical and electrical properties of these films were studied. Photoelectrochemical properties of the films have been studied by forming photoelectrochemical cell. Configuration of the cell was n-WO_3 /0.1 M Na_2SO_4 /C. Some of the physical parameters of the cell like flat band potential, donor density, hole diffusion length were estimated by using Gartner's model for metal electrolyte junction.

The present work is divided into Six chapters. Literature on PEC characterization of WO_3 photoanodes is surveyed in Chapter I and it is found that the physical properties of tungsten oxide semiconductors are strongly dependent on the method of preparation of the material. The large variation in the values of optical band gap and flat band potential appeared in literature seems to depend sensitively on the sample preparation conditions. Purpose of dissertation is also stated in the same chapter. Chapter-II introduces subjects of electrochemistry and solar energy conversion. Chapter-III reports the preparation of F.T.O coated glass substrates and deposition of WO_3 thin films. Optimization of different preparative parameters for obtaining good quality of thin films are also discussed. Structural, optical and electrical properties of WO_3 thin films are studied with the help of various techniques and results are reported in Chapter-IV. PEC properties, viz. I-V characteristics, spectral response, transient photoresponse, C-V characteristics, stability of the cell formed with WO_3 thin film photoanode are explored in Chapter-V. Estimation of physical parameters such as bandgap energy (E_g), concentration of carriers (N_D), flat band potential (V_{fb}) using Gartner's model of the metal-electrolyte junction is discussed in chapter-VI. Detailed summary of the work undertaken is given below.

Deposition of thin films by spraying solutions on to the hot substrates is a simple and low cost technique, by which large number of thin films on variety of substrates (glass, ceramic or metallic) can be prepared. The preparative parametrs were optimized in order to achieve uniform, pin hole free and adhesive films. Tungsten oxide films were prepared on glass and F.T.O.coated glass substrates. WO_3 powder (LR grade B.D.H.Ltd.,) dissolved in hot ammonia solution was sprayed onto the hot substrates. The substrate temperature and spray rate were $250^{\circ} \pm 5\,^{\circ}C$ and 25 cc/min respectively. The concentration of the spraying solution was varied from 0.01 M to 0.05 M. The films were then heated in furnace at $550 \pm 10^{\circ}C$ for 6 hours in order to decompose the tungstate and to get WO_3. Films obtained by this method were found to be of good quality.

Tungsten oxide films prepared at different solution concentrations were subjected to study for their structural, optical and electrical properties. The surface morphology of the films was studied by using transmission optical microscopy. Inspection of these micrographs revealed that the films were uniform and pin hole free. Well defined grain structure of the film was observed from scanning electron micrograph. Grain size of the film, calculated by using Contrell's method was found to be 0.4μ m.

X-ray diffraction studies showed that the films were polycrystalline in nature and consists of mixed monoclinic and triclinic structures.

The IR transmission spectra of the typical film was compared with that of the standard IR spectra of WO_3 and was observed to be similar except an additional peak at wavenumber 720. This additional peak may be related to the traces of WO_4^{-2} ions in the film.

Energy band gaps were estimated by analysing optical absorption spectrographs. E_g varied between 2.62 to 2.42 eV with concentration of sprayed solution. This variation may be related to change in thickness of the film with concentration.

The electrical resistivity of the film were studied with two point probe method. Room temperature resistivity of films decreases with increase in thickness of the film. A remarkable drop in electrical resistivity is observed for films with thickness greater than 1 μ m.The variation of electrical resistivity of the films was studied in the temperature range 300 to 475 K. It was found that resistivity decreases with increase in temperature thereby indicating semiconducting nature. From the grphs of log ρ versus 1/T it was observed that for the films with thickness less than 1 μm a kink is observed at about 375 K. Thus 1 μm thickness was the critical thickness for the electrial properties of the films. The activation energies of the films were estimated and found to be in the range of 0.04 to 0.08 eV. There was no systematic variation in activation energy with the concentration of the sprayed solution.

the photoelectrochemical properties of the cell, n-WO_3 /0.1M Na_2SO_4 /C were studied to obtain an information about charge transfer at semiconductor-electrolyte interface and utilization of the device in the span of solar spectrum.

The current - voltage chacracteristics of the cell were studied the IV curves shifts to the fourth quadrant under illumination which shows n-type semiconducting behaviour.Short circuit current and open circuit voltage at 28 mW/cm^2 illumination intensity were 12 μA/cm^2 and 260 mV respectively. While fill factor and energy conversion efficiency were of the order of 0.28 and 0.003% respectively. The low value of energy conversion efficiency is obvious because of the large band gap of the material. Ideality factors for the cell in dark and under illumination were 9 and 5 respectively. Spectral response study showed that the energy band gap was ~ 2.8 eV. The transient photovoltages were studied at different light intensities and decay time constant ' τ ' was calculated. The decay time constant ' τ ' was of the ordr of 36 seconds, this is an indication of slower hole capture kinetics. The flat band potential determined from Mott-Schottky plot was 0.15 V versus SCE and the value of donor density was 5×10^{16} cm^{-3} .Stability of the WO_3 film in 0.1 M Na_2SO_4 electrolyte was studied and was found that the films were stable for 10 or more hours.

The physical parameters like V_{fb}, N_D, L_p etc. of the PEC cell were estimated by using Gartner's model. The calculated parameters were as follows :

V_{fb} = 0.04 eV

$N_D = 6 \times 10^{16}\ cm^{-3}$

L_p = 0.05 and 0.03 μm for λ = 375 and 425 nm respectively.

E_g = 2.9 eV.

These values are in agreement with values obtained by conventional PEC techniques. The values of V_{fb} determined from the photoresponses, agree within 0.1 V with the values obtained by capacitance measurements using a Mott-Schottky plot. For estimation of V_{fb} the photoresponse measurements are found to be more reliable than capacitance measurement technique which is sensitive to surface states and adsorbed species. The hole diffusion length is small compared to the depletion layer thickness. This is probably due to low mobility factor. The value of band gap energy determined from wavelength dependance was observed to be higher than that obtained from optical absorption study. This discrepancy may be attributed to the different experimental technique employed.