CHAPTER-I

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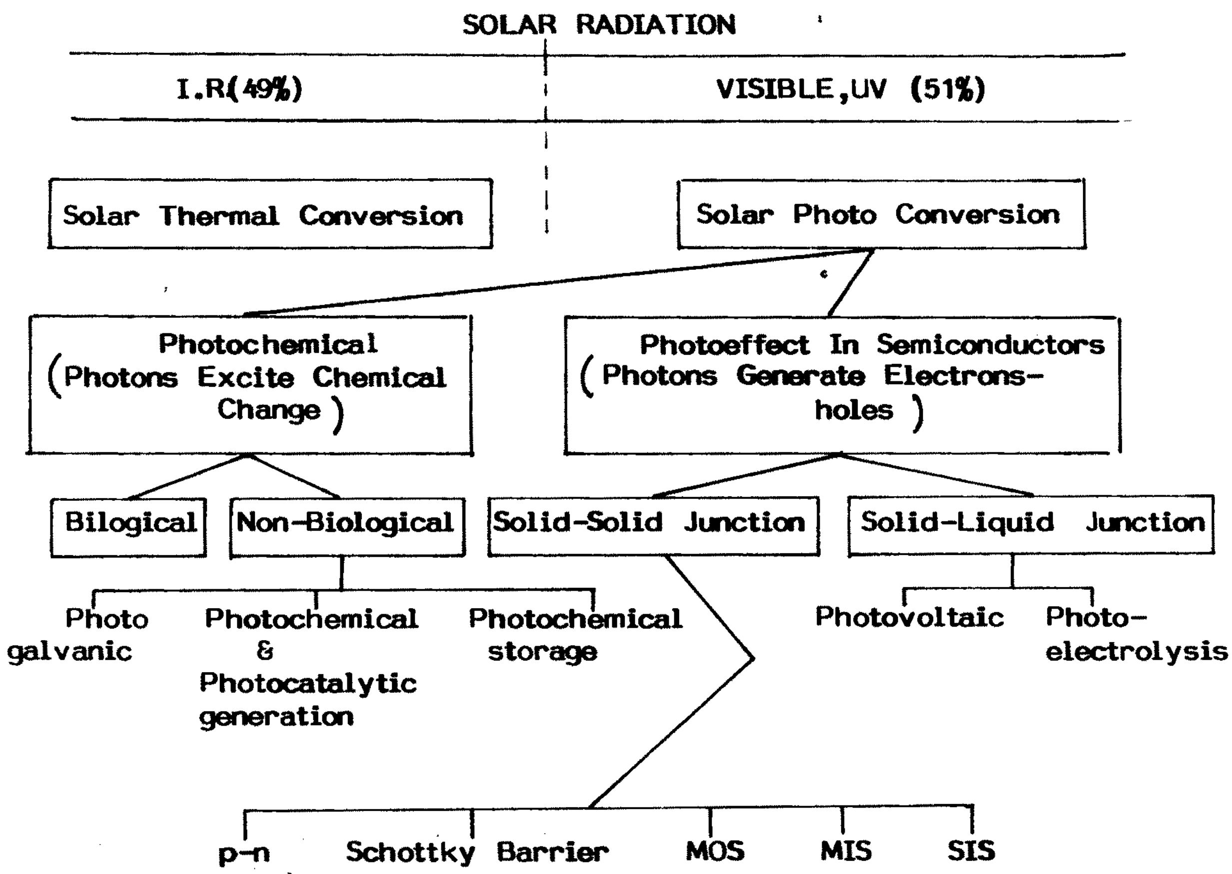
1.1 GENERAL :

'Energy' a fundamental issue to all people, permeates the fabric of human life. In recent years, energy has acquired significant importance due to what has been called, the 'world energy crisis'. For the first time, in the begining of 1970's the rate of reserve discoveries and the rate of consumption growth became inverted alarming that depletion could take place during the next generation. In such a situation the sun, which mankind has regarded as the source of light and energy since time immemorial, drawn attention of scientists as a alternative source of energy to overcome energy crisis.

The most tantalizing feature of the sun's energy is its abundance. The solar flux at the outer edge of the atmosphere is 1.4 kW/m^2 .Although absorption and reflection reduce this, about 50% of it reaches the earth's surface. The noon intensity of solar energy on a clear day in the tropics can exceed a kW/m^2 . This energy falling on an area about 8 km^2 is approximately equivalent to the output of the whole of India's electricity generating system.

The desert areas of the world extend over about 20 million square kilometers. On this area of land, which grows no food and supports no population, the total annual solar radiation is about 400 times the world's present energy consumption . This obvious superfluity of energy, with no known way of collecting more than a tiny fraction of it, makes solar energy research both extraordinarily challenging and maddeningly frustrating.

The most commonly used devices for collecting solar energy can be classified as follows :-



Much effort has recently been directed towards developing new and better solar energy conversion devices. In the 1970's, an inovative strategy was suggested in which a solid-liquid junction was used. Here, instead of the solid-solid junction of conventional solar-cells, a semiconductor electrode dipped in a liquid electrolyte provided the necessary charge transfer, a redox ionic species being used to obtain photovoltage/photocurrent. In 1972 Fujishima and Honda [1] used such an approach to photoelectrolyse water and thus obtained hydrogen (a transportable form of energy); in 1975, Gerischer succeeded in the direct conversion of solar energy into electricity, a strategy that offers the possibility of both solar energy conversion and storage : Photoelectrochemical solar cells. In recent years, semiconductor-electrolyte junction solar cells have been attracting a great deal of interest in the field of solar energy conversion, as they have many advantages over the conventional p-n junction or Schottky barrier cells [3-7]. i) Easy and simple to make. (ii) Many processing steps of the p-n junction cell are simplified or eliminated. (iii) Growth of large single crystals is not required, even with crystallites as small as 10-20 μm, a substantial part (70%) of the efficiency of the single crystal based cell is achieved. (iv) Since the junction with the liquid forms spontaneously up to contact, irrespective of crystal orientation, randomly oriented crystallites can be used.

v) The doping and diffusion steps, in which p-n junctions are formed, are eliminated. (vi) The need for front metallization is eliminated, since the current is carried by the redox couple in solution and the inexpensive counter electrode. (vii) A transperent epitaxial layer, which is grown to reduce electron-hole surface recombination losses at the surface is not needed. (viii) Anti-reflection coating can be replaced by building a non-reflective structure into the surface of a semiconductor by simple etching.

Semiconductor-electrolyte cells may be of two types, one directed primarily at the production of electricity and other making chemical products through a chemical change in the electrode or electrolyte. Reviews of extensive **investigation** of the electrochemistry of semiconductor materials and their photoeffects have appeared in the **literature** [7-9].

1.2 SURVEY OF LITERATURE ON TUNGSTEN OXIDE THIN FILMS AS A PHOTOANODE IN PEC CELL :

Studies on trungsten oxide thin films as a semiconductor photoanode in PEC cell have been reported by several authors; some of which are cited below.

A systematic study of the optical and electrical properties of thin films of WO_3 was made by S.K.Deb [10] for the first time. The measurements were made on number of physical properties such as the structure, optical absorption spectra, refractive index, electrical conductivity, photoconductivity and colour centre formation by optical irradiation and electric field. He reported the band gap energy determined by optical absorption method as 3.25 eV.

Gary Hodes et al [11] prepared WO_3 films by heating tungsten metal to form WO_3 layer and by thermal decomposition of ammonium tungstates sprayed onto the substrate and reported that WO_3 with band gap energy 2.8 eV is the stable electrode, in 1N H_2SO_4 electrolyte, which can be used in PEC cells for solar energy conversion.

M.A.Butler et al [12] used single crystals of WO_3 grown by vapour transport and found that WO_3 is stable electrode with a proper choice of electrolyte and have reported on investigations of tungsten trioxide as an electrode for photoelectrolysis of water. Band gap reported is 2.7 eV. Using single crystals of WO_3 and 1M sodium acetate electrolyte M.A. Butler [13], treated semiconductor-electrolyte junction as simple Schottky barrier, and the photocurrent is described by using Gartner model [2]. It is shown for WO_3 that minority carrier diffusion plays a limited role in determining the photoresponse of the semiconductor-electrolyte junction. It is also shown that the band gap energy depends relatively strongly on applied potential and electrolyte.

In a survey of 'photoelectrochemical behaviour of several polycrystalline metal oxide electrodes in aqueous solutions'. Hardee and Bard [14] prepared WO_3 films by (i) Chemical vapour deposition, (ii) Evaporation of solution on substrate and (iii) Direct oxidation of metal, and found that films prepared by CVD and solution evaporation are stable enough for water oxidation. From the photocurrent versus wavelength curves for films prepared by all methods they observed an absorbancy begining at wavelengths corresponding to about 2.6 eV and also stated that the shift in the peak location, must represent structural or compositional differences between the polycrystalline and single crystal materials. In addition to this they have also suggested that, one approach to finding useful materials may involve modification of the structure or composition of TiO_2 ,Fe_2O_3 and WO_3 by introduction of impurity bands or the formation of ternary compounds involving these.

Gissler and Memming [15] have prepared films by sputtering as well as thermal oxidation of tungsten sheets and obtained $WO_{2.98}$ composition. They reported V_{fb} equal to 0.2 V versus SCE for sputtered layer and -0.55 V versus SCE for thermally grown WO_3 and also pointed out that V_{fb} is slightly changed by the heat treatment.

The semiconducting properties of amorphous WO_3 anodic films grown in different solutions and at different current densities have been investigated by F.Di Quarto et al [16]. They concluded that the value of the flat band potential obtained by Mott-Schottky plots are more reliable only for the specimens with low density of surface states. They also estimated the value of flat band potential by using Gartner's model.

the photoelectrochemical behaviour of amorphous anodic films grown on tungsten have been studied by F.Di Quarto et al [17]. the experimental results are interpreted on the basis of the semiconducting properties of the film and by taking into account the various mechanisms of transport occuring in amorphous materials and they emphasized that a photoelectrochemical study of the amorphous semiconductor-electrolyte interface can be a valuable tool in obtaining further knowledge of the electronic properties of these materials.

K.Miyake et al [18] investigated the electrical and optical properties of reactively sputtered tungsten oxide films in relation to the oxygen concentration in sputtering atmosphere. They found that electrical resistivity and spectral transmittance of the films formed depend extremely on the oxygen concentration in the atmosphere. Optical band gap was found to be 3.02 -3.03 eV.

1.3 PURPOSE OF DISSERTATION :

Tungsten oxide semiconductor films have been studied extensively as a photoanode and reviewed in section 1.2. Of the three fundamental properties of solar cells that define their ultimate practicability– efficiency, cost and stability (life time)– stability is probably the most important. For some specific applications, cost or efficiency may not be of primary importance, but if a solar cell is not reasonably stable, a battery will serve its purpose as well, or better. Some oxide semiconductors are proved to be stable in PEC cells. Good chemical stability and easy preparation makes WO_3 an interesting material for applications in semiconductor-liquid junction solar cells.

Survey of literature reveals that the physical properties of tungsten oxide semiconductors are strongly dependent on the method of preparation of the material. The large variation in optical band gap and values of flat band potentials appeared in literature seems to depend sensitively on the sample preparation conditions.

In the present work it is planned to prepare WO_3 films by employing spray pyrolysis technique. It is one of the simple methods to coat the desired semiconducting film at low cost on large areas with good quality. Very few attempts have been made to prepare WO_3 semiconductors by this technique. The properties of films can be varied by changing the deposition parameters, which facilitates the preparation of films with desired properties. These films have been deposited by spray pyrolysis technique having all preparative parameters, like substrate temperature, spray rate, concentration of spraying solution etc, optimised. These films have been characterized by means of structural, electrical and optical measurement techniques.

The PEC cells are formed by employing these films as photoelectrodes. The cell properties such as, current-voltage characteristics, capacitance voltage characteristics, spectral response, transient photoresponse and stability of the cell are studied. Use of Gartner's theory is made to estimate some physical parameters of the semiconductor thin film.

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