CHAPTER - VII

SUMMARY AND CONCLUSIONS

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Photoelectrochemical solar cell is an attractive system because it offers an opportunity to store the solar energy in the form of a 'fuel', which is easily transportable. Much attention is given to the fabrication and modification of PEC cells with new semiconducting materials.

Among all the chemical methods, electrodeposition is more advantageous such as less expensive, simple and easily controllable deposition parameters.

In view of this, in the present research work, thin films of molybdenum diselenide (MoSe$_2$), tungsten diselenide (WSe$_2$) and molybdenum tungsten diselenide (Mo$_x$W$_{1-x}$Se$_2$) have been prepared on TCO coated glass substrates and on conducting titanium plates by pulse electrodeposition method under galvanostatic condition. Optimization of the film preparation has been carried out by varying the deposition parameters such as composition, concentration of the electrolyte bath, pH of the solution, deposition current, temperature, time of deposition and duty cycle. The films were annealed in vacuum to improve the crystallinity (grain size). Characterization of the film has been carried out by XRD, SEM, AFM, EDAX, capacitance-voltage measurements, electrical and optical studies. Further the
photoactivity of the pulse electrodeposited films prepared under optimized conditions is tested by constructing PEC solar cells after selecting the proper redox couple.

The salient features of the various studies carried out and the important findings are presented.

A thorough literature survey for MoSe$_2$, WSe$_2$ and Mo$_x$W$_{1-x}$Se$_2$ compound thin films is presented in chapter I. The theoretical background and the electrochemistry behind the electrodeposition technique are presented in Chapter II. The growth kinetics method is used to fix the deposition parameters. The films prepared are confirmed first by the colour observation and then by taking XRDs. The optimized pulse electrodeposition parameters used to prepare MoSe$_2$, WSe$_2$ and Mo$_x$W$_{1-x}$Se$_2$ ($x = 0.25$, $0.50$ and $0.75$) are presented in chapter III. The films synthesized under optimized conditions are found to be smooth, uniform, pin hole free and well adherent to the substrate.

XRD patterns of Mo$_x$W$_{1-x}$Se$_2$ ($0\leq x \leq 1$) films show polycrystalline nature and are hexagonal structure. The preferential orientation is along (1 0 2) direction for asdeposited and vacuum annealed films. The asdeposited films show poor crystallinity and it is improved when it is vacuum annealed. The deposition temperature in the range of 30 - 65°C is found to be optimum for the deposition of device quality Mo$_x$W$_{1-x}$Se$_2$ thin films.

EDAX study confirms the elemental presence of Mo, W and Se on the films. The atomic weight percentages of these elements prepared under optimized conditions are near stoichiometric.
SEM pictures show uniform granular shaped grain size without pinholes. The grains are closely packed and surface is smooth. Annealing of films in vacuum improves the surface smoothness. The grain size also increases from about 0.84 to 0.94 µm for the pulse electrodeposited films.

AFM pictures show the presence of hills on the top of a homogeneous granular background surface. This observation reveals that the growth of Mo_xW_{1-x}Se_2 films on tin oxide substrates by pulse electrodeposition is associated with the formation of three-dimensional grains in the perpendicular direction without lateral diffusion of adatoms on the surface parallel to the substrate. This may be attributed to the preferentially oriented crystalline nature of the TCO coated glass substrate over which Mo_xW_{1-x}Se_2 films are deposited.

An indirect band gap value of about 1.16 eV is observed for MoSe_2 films and 1.42 eV for WSe_2 films. The band gaps for the solid solution Mo_{0.25}W_{0.75}Se_2, Mo_{0.5}W_{0.5}Se_2 and Mo_{0.75}W_{0.25}Se_2 are 1.30 eV, 1.25 eV and 1.53 eV respectively. The values of the optical constants n and k lie in the range of 2.82 - 4.07 and in the range of 0.59 x 10^{-9} - 0.11 x 10^{-3} respectively in the wavelength range 300 to 1200nm for all Mo_xW_{1-x}Se_2 films.

The resistivity of Mo_xW_{1-x}Se_2 solid solution decreases with increasing molybdenum and tungsten content x. p-type nature is observed for all films, which is attributed to nonmetallic excess on the surface of the films. The activation energies E_a of these films are in the range of 0.06 - 0.96 eV, the trapped energy states e are in the range of 0.110 - 0.62 eV and the barrier height \phi_0 are in the range of
0.11 - 1.18 eV respectively. These values are nearly equal to the optical band gap value, which confirms the presence of the acceptor level close to the conduction band edge in p-Mo$_x$W$_{1-x}$Se$_2$ films.

The photoelectrochemical behaviour of the Mo$_x$W$_{1-x}$Se$_2$ and Mo$_{0.5}$W$_{0.5}$Se$_2$ films in the electrolyte 0.2 M KI / 0.05 M I$_2$ is found satisfactory in which the photoactivity is maximum and the layers are highly stable. From the nature of the Mott-Schottky plots, it is found that all the films are p-type in nature. The acceptor concentration ($N_A$) for the films is in the order of 10$^{18}$ cm$^{-3}$. The depletion layer width ($W$) of Mo$_x$W$_{1-x}$Se$_2$ films was in the range 0.432 to 0.760 µm. The maximum value of Voc and Isc occurs for annealing in vacuum for the temperature of 150°C for 1 hour for MoSe$_2$, WSe$_2$ and Mo$_{0.5}$W$_{0.5}$Se$_2$ films. The conversion efficiency of MoSe$_2$ film is 0.189%, WSe$_2$ films are 0.123% and Mo$_{0.5}$W$_{0.5}$Se$_2$ films are 0.490% respectively.

The low efficiency of the cell could be due to the low carrier concentration. It may also be attributed to the fact that the films might have high densities of surface states and grain boundaries, which can act as recombination centres for photogenerated carriers. The solid solution Mo$_x$W$_{1-x}$Se$_2$ prepared by pulsed electrodeposition method is found to show good stability against photocorrosion.

The PEC parameters for the PEC cells fabricated using Mo$_x$W$_{1-x}$Se$_2$ films were calculated. Based on these studies it may be observed that electrochemical routes can produce device quality semiconductor films useful for solar energy conversion.
7.2 SUGGESTIONS FOR FUTURE WORK

The long term dream of providing a pollution free energy to mankind for all purposes would be fulfilled if the reduction in the cost of the solar cells with good efficiency is achieved through thin films and by identifying the choice of the material for the same. Alloying and doping are the ways to get the suitable potential compound that can realize this dream.

It is suggested that it would provide a wealth of results and informations if attempts are made to identify theoretically the best composition of alloy thin films of IV – VI compounds for better PEC / PV performance and to synthesize the particular compound using electrosynthesis. The effect of doping ions like N₂, He, P etc. using methods like ion implantation on these compounds may be studied. New solid solution may be prepared incorporating Cd, Pb and Zn to these compounds, which may improve the efficiency of the PEC cells.