P R E F A C E

Over the last two decades a great deal of interest has developed in the area of photoelectrochemistry, particularly in the application of photoelectrochemical systems to the problem of solar energy conversion and storage. The interest is to develop new energy sources to supplement and eventually replace fossil fuels.

One of the newest research areas related to solar energy conversion, which is currently exciting much interest and activity, is the study of photoelectrochemical devices. Two classes of photoelectrochemical devices can be defined : photoelectrolysis cells and semiconductor electrolyte photovoltaic cells. In the former, optical energy is converted into chemical energy by the photodecomposition of water into H_2 and O_2. In the latter, optical energy is converted into electrical energy as in a conventional, solid state photovoltaic device, except that the internal potential barrier producing charge seperation is created by a solid state p-n or Schottky-type junction. In both of these devices, unique and stringent materials problems must be solved before they can become commercially successful.

The effective use of solar energy in photovoltaic or photoelectrochemical applications depends in part on the development of materials that can show high conversion efficiencies and long term stability under operation. In addition, the desirable materials should have a band gap that closely matches the solar spectrum and be made of readily available and inxpensive materials.

Investigators focussed their attention on the transition metal dichalcogenides (e.g., WSe_2, $MoSe_2$ and others), also known as layered or d-d semiconductors. Single crystals of these materials have been studied extensively in both aqueous and nonaqueous solvents and in photovoltaic and photosynthetic cells. The advantage of using these materials are that they have band gaps (1.1-1.6 eV) that closely match the solar spectrum and exhibit high conversion efficiences as single crystals. In addition, they can achieve long-term stability due to the fact that the transitions are localized in the non-bonding d-orbitals of the metal. These materials consist of metal dichalcogenides sandwitches (e.g., Se-W-Se) held together by Van-der waals forces. The fact that there is strong covalent bonding within the layers, but only weak interactions between layers makes these materials highly anisotropic in their properties. Although single crystals of these materials have shown very high efficiency.

Studies among the n-type single crystals of transition metal dichalcogenides in aqueous electrolytes containing I^-/I_2

revealed that in absolute values as well as in relation to the energy gap n-type WSe_2 could produce the largest photopotential output and was found to be most promising for solar energy conversion applications. From the literature it is observed that the conversion efficiencies so far reported with n-type WSe_2 electrodes are upto 17%.

Since among TMDC's WSe_2 occupies a favourable position with suitable band gap of 1.57 eV and is one of the most promising material in PEC solar cell applications, author has concentrated his efforts on growth of this material in the form of single crystals by using chemical vapour transport method involving different transporting agents. Initially the grown crystals have been characterized by EDAX and X-ray diffraction techniques. Thereafter measurements of their transport properties have been carried out. Finally attempts have been made to fabricate PEC solar cells using the grown crystals as photoelectrodes.

The results of all the above investigations have been compiled in the form of a thesis.

The thesis begins with an introduction on the existing information on tungsten diselenide (WSe_2) single crystals (Chapter-1). The description of growth techniques, describing the chemical vapour transport method and the experimental set up involving temperature controlling system, construction of the furnace etc. have been given in Chapter 2.

The 3rd and 4th Chapters present a brief report on growth and parameters such as growth time, growth temperature, concentration of the transporting agent and size of the crystals etc. have been determined for the single crystals(WSe_2) grown using $SeCl_4$, Br_2, $TeCl_4$ and $SeCl_4$ + Se as transporting agents. The grown crystals have been characterized structurally by determining lattice parameters. The compositions of the as-grown crystals have been examined by EDAX: Study of the microstructures on the as-grown crystals reveals the presence of hexagonal, triangular and circular spirals upon them. The description of the resistivity measurement and the effect of temperature on resistivity have also been incorporated. The Hall coefficient has been determined from Hall effect measurements. The results obtained have been compared with those reported by earlier workers.

A necessary introduction to PEC solar cells is provided in Chapter 5. Different types of solar cells have been described and discussed by giving their classification. Materials requirement for photoelectrochemical solar cells have also been described in detail.

The fabrication of PEC solar cells with n-WSe_2 crystals grown by chemical vapour transport method using Br_2, $TeCl_4$ and $SeCl_4$ + Se as the transporters have been described. The flat band potentials have been estimated to characterize the semiconductor-electrolyte interface in terms of location of valence and conduction band edges. Prior to this the spectral response of the grown crystals has been studied by measuring photocurrent at different wave lengths and direct band gaps have been estimated. Similar experiments and measurements have also been carried out and discussed (Chapter 6 & 7) on p-WSe_2 single crystals grown by chemical vapour transport technique using $SeCl_4$ as a transporter.

Effect of light intensity and electrolyte concentration on the performance of PEC solar cells, i.e. on cell parameters such as open circuit voltage, short circuit current, fill factor and efficiency etc. have been studied on both n-type and p-type WSe_2 electrodes. The results have been described in Chapters 8 & 9.

Chapter 10 describes the dependence of the PEC performance on the surface features of the crystal electrodes. Modifications of the surface features by chemical etching and their effect on the cell parameters have been described.

Chapter 11 deals with the effect of photoetching on the performance of the photoelectrodes.

The conclusions drawn from the present study the scope for further work in the direction are indicated at the end of the thesis (Chapter 12).