ABSTRACT

The thesis entitled "Studies on Electrodeposited and Brush plated SnS_xSe_{1-x} Semiconducting Thin Films for Photoelectrochemical cells" is a report bringing out the preparation, characterization of SnSe, SnS and SnS_xSe_{1-x} thin films by electrodeposition and brush plating techniques and their applications in photoelectrochemical solar cells devices.

Among the many chalcogenides IV-VI semiconductors, tin selenide (SnSe) and tin sulphide (SnS) are isomorphous and crystalline in a rhombic, pseudotetragonal layer structure.

The selenide (SnSe) films have great potentialities in holographic recording, memory switching devices and solar cell applications. Tin sulphide (SnS) is one of the promising materials for low-cost thin film solar cells, since its optical energy gap of 1.1 eV is similar to that of silicon and it might serve as an optoelectronic material. The photoelectrochemical (PEC) behaviour of SnSSe solid solution has been reported. However, the various parameters affecting the PEC behaviours of SnS_xSe_{1-x} with various values of 'x' are not reported in detail in the literature. The aims of the present work are

(a) to prepare thin films of SnSe, SnS and SnS_xSe_{1-x} by the electrodeposition and brush plating techniques and optimize their preparation conditions suitable for device applications.

(b) to study the microstructure and composition of the electrodeposited and brush plated films through X-ray diffraction analysis (XRD), Electron Spectroscopy for Chemical Analysis (ESCA), Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM).

(c) to study the optical behaviour of these films in the ultraviolet, visible and near-infrared regions and the electrical properties of these films.
(d) to explore the feasibility of using SnSe, SnS and SnS\textsubscript{x}Se\textsubscript{1-x} thin films as photoelectrodes in photoelectrochemical solar cells leading to the fabrication of low cost cells for solar energy conversion.

(e) to evaluate the solar cell parameters using computer simulation.

Various techniques of thin film deposition are briefly mentioned and a thorough literature survey is also presented for SnSe, SnS and SnSSe alloy thin films.

As it is the first report to our knowledge on brush plating of compound semiconducting thin films, the basic principles and background of brush plating of metal and alloy are given in detail.

The preparation of thin films is described in detail. The details regarding the experimental set up of electrodeposition and brush plating are described. Cyclic voltammetric studies are carried out to determine the optimum deposition conditions of Sn, Se, S and their mixtures. The influence of hydrogen ion concentration, bath temperature and the concentration of the ionic species on the deposition of the films are studied in detail.

The deposition behaviour of the individual Sn\textsuperscript{2+}, Se\textsuperscript{2-} and S\textsuperscript{2-} ionic species is studied through cyclic voltammetry. Cyclic voltammetric studies reveal that SnS\textsubscript{x}Se\textsubscript{1-x} (x = 0, 0.5 and 1.0) films could be electrosynthesized in the potential range – 700 to –900 mV versus SCE to yield near stoichiometric films. The studies showed that homogeneous solid solutions of SnS\textsubscript{x}Se\textsubscript{1-x} could be obtained, the film composition being altered by the SeO\textsubscript{2} and S\textsubscript{2}O\textsubscript{3} concentration, films are deposited at bath temperatures, 28, 40, 50 and 60°C. It is found that thicker films are deposited at higher bath temperatures which are found to be smooth and more uniform than the films deposited at room temperature.
The structural, compositional and morphological studies carried out on SnSe, SnS and various compositions of SnSₓSnₑ₁₋ₓ films, are presented. The effect of bath temperature, selenium, sulphur ion concentrations, deposition potential on crystal structure of SnSₓSnₑ₁₋ₓ films prepared by both electrodeposition and brush plating methods are thoroughly studied. X-ray diffraction (XRD) and electron spectroscopy for chemical analysis (ESCA) showed that the stoichiometric films with orthorhombic structure are obtained. These studies revealed that the room temperature deposited films are having poor crystallinity and the films are smooth and uniform when the deposition temperature is between 50 and 60°C. The effect of annealing the films in vacuum and in air is studied.

It is found that in the formation of SnSₓSnₑ₁₋ₓ thin film, the variation of S and Se concentration affects the formation of the entire range of solid solution. The films are found to be orthorhombic structure. The effect of annealing on the crystal structure of SnSₓSnₑ₁₋ₓ thin films is studied and the results are discussed.

A similar examination of the effect of selenium and sulphur ion concentration, bath temperature, plating potential, plating time on the structure of brush plated SnSe, SnS and SnSₓSnₑ₁₋ₓ thin films is made.

The morphological examination of the films synthesized by both electrodeposition and brush plating is presented. The film contains dense and closely packed grains, which are well adherent to the substrate as observed from SEM pictures. The average grain size of the films is about 0.5 to 0.8 μm. Atomic force microscopy (AFM) studies show the surface morphology of the films with higher resolution. Average grain size of electrodeposited and brush plated films of SnSe, SnS and SnSₓSnₑ₁₋ₓ is found and reported. The root mean square surface roughness of these films is also determined and reported in this chapter.
In Chapter V, the optical and electrical properties of electrodeposited and brush plated SnSe, SnS and SnSₓS𝚎₁₋ₓ thin films are presented. An absorption edge at 1100 nm corresponds to a bandgap value of about 1.03 eV for the SnSe films which is in good agreement with the reported value. The bandgaps for SnS and for the solid solution of SnSₓSє₁₋ₓ thin films are about 1.2 and 1.12 eV respectively. The optical constants n and k of the SnSₓSє₁₋ₓ thin films are estimated using an improved continuous differential descent method. The variation of n and k with wavelength is discussed. The electrical properties of electrodeposited and brush plated SnSₓSє₁₋ₓ films are discussed. It is found that the resistivity of SnSₓSє₁₋ₓ thin films decreases with x. The activation energies of these films are estimated and the results are discussed.

The fabrication and studies of photoelectrochemical (PEC) solar cells based on the films prepared by both techniques are described. The performance of SnSe photoelectrode is found to be strongly dependent on the deposition potential. The photoelectrochemical properties of these films are studied using different electrolytes like 0.1 M (Na₂S-S-NaOH); 0.1 M (KI-I₂); 0.1 M [K₃Fe(CN)₆ - K₄Fe(CN)₆] and 0.1M (FeCl₂ – FeCl₃), 0.05 M H₂SO₄. It is found that 0.1 M (FeCl₂ – FeCl₃), 0.05 M H₂SO₄ is the most suitable electrolyte which shows photoactivity and the layers are very stable in this electrolyte.

The current-voltage curves are obtained for SnSe, SnS and SnSₓSє₁₋ₓ films in dark and under illumination. The curves obtained under illumination are shifted from that for dark, which indicates the photosensitivity of the films. A photoelectrochemical cell using electrodeposited film as photoelectrode with the configuration of p-SnSe [Fe³⁺,Fe²⁺] Pt yields a conversion efficiency of 0.19% and p-SnS [Fe³⁺, Fe²⁺] Pt cell yields an efficiency of 0.31%. A slightly enhanced conversion efficiency is found for the brush plated films. The solid solution SnSₓSє₁₋ₓ prepared by both electrodeposited and brush plated methods is found to show good stability against photocorrosion.
A computer program has been developed to simulate and to extract the five parameters of the cell; open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), series resistance ($R_s$), shunt resistance ($R_{sh}$) and diode factor ($A$). The program is capable of calculating the fill factor ($ff$) and conversion efficiency ($\eta$) using the above simulated parameters.

Capacitance-voltage measurements are carried out under reverse bias conditions on electrodeposited and brush plated SnS$_x$Se$_{1-x}$ films. Mott-Schottky plots are drawn between $1/C^2$ and $V_{SCE}$. From the nature of the curve it is found that SnS$_x$Se$_{1-x}$ films exhibit p-type conductivity. The associated semiconductor parameters like acceptor concentration ($N_A$), density of states in the valence band ($N_V$), band bending ($V_B$), depletion layer width ($W$) and carrier type are reported.

The quality of the films prepared by electrodeposition and brush plating is compared for the application of photoelectrochemical solar cells. The optimum condition required for film preparation and annealing to obtain high efficiency photoelectrochemical solar cells are discussed.