CHAPTER-VI

C H A P T E R - VI

SUMMARY AND CONCLUSIONS.

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Todays technology requires various types of thin film materials which are assuming increasingly interest for a variety of applications. A single or multicomponent, mixed, alloy/compound or multilayered coatings on substrates of different sizes and shapes may form a thin film structure. Depending on the applicability, the properties such as high optical reflection/transmission, hardness wear resistance, single crystal nature etc. of the thin films are required. Such versatility in thin films can be brought about by the techniques of the thin film deposition. Although these thin films are generating continuous interest their structure is complex in view of their application which demand taylor made properties. As a result, sophisticated characterisation tools have emerged out for understanding of the multifarious properties of thin films. A host of characterisation techniques are available, depending on the property and interest, for giving some times similar and more often additional and complementary informations. Further, the properties of the film have a direct bearing on a method of formation and it is quite obvious that no one technique can deposit the film which can suffice all the problems. The different commonly used thin film deposition techniques are overviewed in chapter II (section 2.2.) . The thin films of II-VI and III-V compound semiconductors are rigorously studied owing to their proven potential ability in manyfold applications.

The chalcogenides of bismuth, arsenic and antimony exhibit excellent electrical, chemical and optical properties which enabled them one of the promising candidates in the field of photovoltaic energy conversion. Thus the choice lies both for the quality of the material and its method of formation. We have selected bismuth trisulphide as a working material owing to its feasibility as a best energy converter (best bandgap match with the solar spectrum, high optical absorbance, direct type of transition etc.). The criterions for the selection of a material are outlined in chapter I (section 1.2.1.). In addition, the process by which it is formed is a simple and easier. Some of its inherent advantages over the other conventional preparative methods are mentioned in sec. 2.3.1. In order to come out of the energy crisis, solid-liquid junction cells are todays alternative to the solid-solid junctions. The solid - liquid junctions have certain favourable advantages over their solid - solid counter part as stated in chapter I. The basic requirements for a good photoelectrochemical cell is also given in section 1.2 . Chapter II describes the different basic charge transfer process at both the electrodes in dark and under illumination. The basic requirements, essential designs, and fabrication of various measurement tools needed to examine various aspects of thin film as well as the photoelectrochemical cells are discussed in chapter III. Chapter IV deals with some of the structural, electrical and optical aspects of the bismuth trisulphide thin films and their comparison with the observed available data. Chapter V lights out some of the interesting results such as electrical and optical properties of the photoelectrochemical cells.

The thin film deposition process developed in our " Thin Film and Solar Cell Research Laboratory ", for the deposition of chalcogenides of bismuth, antimony, arsenic cadmium, silver, lead, tin etc. and some alloyed compositions thereoff,with suitable impurity concentration is found to be convenient, simple, easier and reproducible one in which good quality, uniform , large area and adherent deposits on various substrate materials can be obtained. As has been mentioned earlier (to start with) thin film deposits of bismuth trisulphide were grown onto the amorphous ground glasses and stainless steel supports by a chemical deposition process. The basic materials used were triethanolamine complex of bismuth, thiourea, and NH_4OH. The various preparative conditions and parameters are optimised in the initial phases of the work. The selected values of these parameters are :

i) Temperature of the deposition - 95± 2 ^{o}C .

ii) Speed of the substrate rotation - 70 r.p.m.

iii) Time for the deposition - 40 min.

iv) Substrate holder geometry.

v) pH of the reaction mixture = 9.5.

The work that has been carried out is splitted into four steps as under :

I) Preparation of $Bi_2 S_3$ Thin Films.

Thin films of bismuth trisulphide have been deposited onto the glass substrates by allowing thiourea to react with a triturated triethanolamine complex of bismuth nitrate. To increase the adherence of the samples on the support ammonium hydroxide was added into the reaction mixture. The chemical reaction can be given as |44|:

$$Bi\left[N(CH_2 \cdot CH_2OH)_3\right]^{3+} + S=C\begin{matrix} NH_2 \\ NH_2 \end{matrix} \longrightarrow Bi_2S_3 + O=C\begin{matrix} NH_2 \\ NH_2 \end{matrix} + n \cdot A \qquad \ldots\ 6.1$$

where, A = complexing agent, N (CH_2, CH_2OH).

The pH of the solution was maintained around 9.5. The temperature of the reaction mixture was controlled to $95 \pm 2\,^{\circ}C$. The film growth can take place by ion-by-ion condensation of the material or by adsorption of the colloidal particles from the solution on the substrate |40,42,43|.

II) The Design and Fabrication Aspects :

The bismuth trisulphide thin films deposited should be ree from all the atmospheric hazards such as contamination, humidity, dust particles etc. A protective means, called as dust proof chamber was designed and fabricated in our laboratory and whole the working assembly was put into the chamber. Other essentials related to the work such as bushing arrangements to the constant speed motor, design of a substrate holder, design of a reaction mixture holder, design and fabrication of electrical conductivity and thermoelectric power measurement units, design and fabrication of photoelectrochemical cell, experimental arrangements for cell properties in dark and in light were procurred and fabricated. In order to protect the photoelectrochemical cell from dust particles, atmospheric gases, humidity etc., a solar cell testing chamber of the approximately same dimensions as that of dust proof chamber was designed and all the photoelectrochemical studies have been carried out under the dust proof conditions. In order to avoid the heating of a photoelectrochemical (PEC) cell by the I-R radiations, an arrangement is done against such heating.

III) Properties of Thin Film Bi_2S_3 :

Since the Bi_2S_3 films were supposed to be utilised as the photoelectrode in PEC cell, it was worth to study the structural, electrical transport and optical properties of the deposits. Much more informations can be obtained from such studies.

i) Electrical transport properties :

As pointed out earlier, the films prepared by this technique are relatively resistive than the other sophisticated preparation techniques. The films have been characterised by the conductivity and thermoelectric power measurement techniques in the temperature ranges 300 to 600 K and 300 to 500 K respectively. The variation of conductivity with temperature suggests that the films are semiconducting and obeys the relation :

$$\sigma = \sigma_0 \cdot exp.(-E_a/kT) \quad \text{... 6.2.}$$

The resistivity of the thin films at the room temperature is of the order of 10^9 ohm - cm. The activation energy calculated from the log. σ vs. 1/T variation is of the order of 0.8[illegible] eV and 0.16 eV respectively, in the high and low temperature regions. The thermovoltage measurement showed that the samples are of n- type and dominant charge carriers are electrons. The order of thermoelectric power (TEP) is in μV. The optical microscopy and X-ray diffraction studies revealed the polycrystalline nature of the samples.

ii) Optical Properties :

The optical absorbance studies were carried out in the wavelength range 4000 Å to 9000 Å . The optical absorption coefficient (α) is of the order of 10^4 cm^{-1}. indicating the direct type of transition. The bandgap was estimated from these results and is 1.60 eV which matches closely with the solar spectrum.

IV) Electrochemical Behaviour of n - Bi_2S_3 Based Photoelectrochemical (PEC) Cells :

The photoelectrochemical (PEC) cells were constructed with n-Bi_2S_3 as a photoelectrode , a mixture of equimolar NaOH -Na_2S -S as an electrolyte and CoS treated graphite rod as a counter electrode Some of the cell properties in dark and in light are recorded.

i) The current - voltage and capacitance - voltage characteristics in dark:

In view to understand the basic charge transfer processes across the electrode / electrolyte interface, the interface properties, namely,I-V and C-V in dark have been examined. Assuming S/E interface as the analog of the M/E interface, Butler Volmer relation |59| was used to describe the current transport mechanism across it . The junction is found to be of the rectifying nature and is analogous to the Schottky barrier junction. The junction ideality factor in dark (n_d) was calculated and it seems that the I - V characteristics in dark are often influenced by recombination and series resistance effects |41,111,114|. The n_d is higher than its ideal value, which indicates the presence of surface states at the electrode/electrolyte interface. The flat band potential, V_{fb}, was determined from the capacitance - voltage measurement studies and is - 0.7 V for the cell formed with n- Bi_2S_3 photoelectrode. This is in close agreement with the results of Pawar et.al |26|. A slight departure from the straight line behaviour has been observed indicating the presence of surface states |41,72|.

Barrier height was determined from the temperature dependence of reverse saturation current of a junction and is of the order of 0.143 eV.

ii) Photovoltaic properties :

The junction is characterised in light under 100 mW/cm^2 intensity and the various cell parameters such as series and shunt resistances (R_s and R_{sh}), fill factor (ff), efficiency (η), short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were examined.

iii) Optical properties :

The measurements on photoresponse, spectral response and speed of response were carried out. The lighted ideality factor (n_L) was calculated from the variation of $\ln.F_L$ vs. V_{oc} measured under different illumination intensities. n_L is found smaller than n_d and is directly related to V_{oc} as |41| :

$$V_{oc} = \frac{n_L \cdot KT}{q} \ln. \frac{I_{sc}}{I_0} \qquad \ldots 6.3$$

where, $I_{sc} \propto F_L$ .The spectral response measurements observed for different wavelengths showed the rapid decay of I_{sc} with wavelength both on shorter as well as longer wavelength sides. The decrease in I_{sc} on shorter wavelength side is attributed to the absorption of light in the electrolyte and the surface recombination centres and to damages or impurities in the bulk very near the surface |41,123| . A reduction in the short circuit current on the longer wavelength side can be caused due to the transitions between the defect levels |41|.

The observed values of cell parameters are :

i) V_{oc} = 160 mV,	vi) η = 0.012 %,
ii) I_{sc} = 0.20 mA/cm^2,	vii) n_d = 3.22,
iii) R_s = 400 Ω,	viii) n_L = 2.49,
iv) R_{sh} = 1600 Ω,	ix) V_{fb} = -0.7 Volt(vs.SCE),
v) f.f = 33.15 %,	x) ϕ_B = 0.143 eV.

Conclusions :

It has been seen from the above studies that the efficiency observed is well below the expectation. The major reasons are : 1) Thinness of the sample ii) absence of the thorough post preparative treatments iii) absorption of the light by the electrolyte. iv) reflection from the glass and from the photoelectrode surface, and v) higher resistance of the sample. Attempts are in progress to overcome these difficulties.

v) Work in Progress and Future Directions : (Beyond the scope of this dessertation)

Bismuth trisulphide layers in its thin film form are highly disordered and grain size is probably a function of distance from the substrate surface . The large number of defects in the active region of thinner Bi_2S_3 may be one of the main causes for the deterioration of the collection efficiency. Thus it is advisable to increase the layer thickness and to observe its reflections especially on cell properties. Surface modifications may also help in improving the quality of the cell performance.

Like the solid state solar cells, earlier methods for the enhancement in the open circuit voltage and short circuit current of a PEC cell have relied on coupling of two separate diodes those respond to two different regimes of the solar spectrum |111,125|. Thus a connection of two diodes in series, in order to boost both the open circuit voltage and short circuit current is a need. Attempts are in progress to improve the performance and hence the quality of a photoelectrochemical cell.