CHAPTER – 6

EFFECT OF INDIUM AND ANTIMONY DOPING ON SnS PHOTOELECTROCHEMICAL SOLAR CELLS

6.1 Introduction

The low cost energy conversion by photoelectrochemical (PEC) solar cells has generated greater interest due to its easy fabrication and the possibility of in situ storage [1, 2]. In recent years, the interest in PEC has been to search extensively for the most suitable materials [3–6] to be used as photo electrodes. Single crystalline materials have found most favor as the electrode material. Tin sulfide, SnS, is a layered semiconductor compound belonging to IV–VI groups, and it is a promising candidate in the field of PEC solar energy conversion due to its high absorption coefficient and stability [7]. Also, the valence band energy of the stable orthorhombic phase of SnS reveals a low ionization potential (4.7 eV) in comparison to typical absorber materials (CdTe, CuInSe₂, and Cu₂ZnSnS₄) [8]. The usage of SnS in solar cells has attracted much interest, since its optical bandgap of 1.08 eV is similar to that of silicon [9]. In layered type SnS chalcogenides, the atoms in a single layer are joined to the three nearest neighbors by covalent bonds which form zigzag chains along the b-axis while there is only van der Waals bonding between the layers, the c-axis. The tailoring of electrical transport properties of base material SnS can be carried out by using different dopants [10–16]. The most suitable dopants are indium(III), In³⁺, and antimony(V), Sb⁵⁺, due to the near matching of its ionic radii to Sn²⁺ cation of SnS. In this chapter, I report the PEC solar cells fabricated using pure SnS, indium (In) and antimony (Sb) doped SnS single crystals as electrodes. Two doping concentrations of 5 at.% and 15 at.% are employed for both In and Sb dopants. Thus in total five samples are studied, viz., pure SnS, 5 at.% In doped SnS, 15 at.% In-doped SnS, 5 at.% Sb-doped SnS and 15 at.% Sb-doped SnS.

6.2 Experimental details

All the single crystal samples viz pure SnS, 5 at.% In doped SnS, 15 at.% In-doped SnS, 5 at.% Sb-doped SnS and 15 at.% Sb-doped SnS were grown by the direct vapor transport (DVT) technique. The as grown single crystal samples were comprehensively characterized before use in PEC. The complete DVT growth run and the characterization results are presented and discussed in Chapter 5. The as grown single crystals were used as electrodes in the photoelectrochemical (PEC) solar cell without any treatment or modification.
6.2.1 PEC solar cell fabrication

The PEC solar cells were fabricated by using the as-grown pure SnS, In-doped SnS and Sb-doped SnS (both doping concentrations of 5 at.% and 15 at.%) as working semiconductor electrodes and a platinum grid of area 1 cm$^2$ as a counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode. The literature shows that the earlier solar cells fabricated with SnS involved the use of Fe$^{3+}$/Fe$^{2+}$ electrolyte [17]. In the present study of PEC, I used pure SnS and SnS that has In and Sb dopants using iodine/iodide (I$_2$/I$^-$) as electrolyte.

Different concentrations of electrolytes were prepared by mixing various concentrations of reagent grade I$_2$, NaI, Na$_2$SO$_4$ and H$_2$SO$_4$ in double distilled water to obtain a diverse composition of iodine/iodide (I$_2$/I$^-$) electrolytes. Mott–Schottky plots were obtained by measuring the capacitance across the cells at different d.c. bias voltages for these prepared electrolytes. From the evaluation of the flat-band potential and the subsequent location of the valence band edge and the redox level from the Mott–Schottky plots, it is found that the electrolyte having a composition of 0.025M I$_2$+1M NaI+2M Na$_2$SO$_4$+0.5M H$_2$SO$_4$ would be the most suitable one for the present single crystal samples. The distance between the semiconductor photoelectrode and the counter electrode was kept to be constant of 1 cm.

6.3 Results and discussion

The SUNLUX 1000W/250V tungsten filament halogen lamp was used for illuminating the respective electrodes. The intensity of illumination was altered by changing the distance between the light source and the electrode. The intensity of illumination was measured each time by a Luxmeter (TES Electrical Electronic Corporation, TES 1332 A). Photocurrents and photovoltages were recorded by using a digital multimeters (Protek, 506 & RISH multimeter, 18 S). The variation of conversion efficiency (%) and fill factor (FF) with light intensity for all the five SnS single crystal samples are shown in Fig. 6.1.
Efficiency ($\eta\%$) and FF versus intensity for (a) pure SnS, (b) 5 at.% In-doped SnS, (c) 15 at.% In-doped SnS, (d) 5 at.% Sb-doped SnS, and (e) 15 at.% Sb-doped SnS single crystals.

It is seen from Fig. 6.1 that the values of conversion efficiency ($\%$) show a linear decrease with the increase of incident light intensity from 10 to 70 mW·cm$^{-2}$. This behavior is common in all the five studied samples. This behavior is in conformity with the reported behavior for doped semiconductors \cite{18}. In the case of FF variation with incident light intensity (10 to 70 mW·cm$^{-2}$) of all the five samples, no regular behavior was observed. The FF (<1) indicates the extent of deviation from the ideal $I$–$V$ behavior. Thus the samples having different In and Sb doping concentrations in SnS show different FF variations with incident light intensity, demonstrating that the magnitude of the $I$–$V$ deviation with intensity is different for different doping concentrations. This means that different dopants behave differently at different incident light intensities.
The comparative analysis of efficiency (%) curves reveal that the In-doped SnS shows better performance than pure SnS and Sb-doped SnS single crystals. The better efficiency (%) of In-doped SnS is seen for both the concentrations of In, i.e., 5 at.% and 15 at.% compared to other samples. The increased efficiency in In-doped SnS is due to the dopant impurity incorporating levels near the top of the valence band and modifying the energy band of the host crystal, which enhances the charge carrier transfer from valence to conduction band \[19\] thus enhancing efficiency (\(\eta\)%). Contrary to In-doped SnS crystals, the Sb doped SnS crystals do not show enhanced efficiency. This may be due to a larger mismatch of the ionic size of dopant Sb\(^{+3}\) (0.90 Å) to host Sn\(^{+2}\) (0.93 Å) compared to dopant In\(^{+3}\) (0.94 Å). Due to this larger mismatch between dopant Sb\(^{+3}\) and host Sn\(^{+2}\), larger strain is observed in the Sb-doped SnS crystals, leading to larger dislocations and defects compared to In-doped SnS (Chapter 5). The presence of larger defects and strains decreases the efficiency of Sb-doped SnS PEC.

6.4 Conclusions

The conclusion drawn from the study of PEC with five DVT grown single crystal samples, viz. pure SnS, In and Sb-doped SnS (doping concentration of 5 at.% and 15 at.% for each dopant) with iodine/ iodide (I\(_2\)/I\(^-\)) electrolytes are as follows: Mott–Schottky plot analysis states that 0.025M I\(_2\)+1M NaI+2M Na\(_2\)SO\(_4\)+0.5M H\(_2\)SO\(_4\) is the most suitable electrolyte for the present single crystal samples and the In doped SnS shows better efficiency than other samples. The efficiency enhancement in In-doped SnS is due to the energy band modification by the formation of an impurity level near the top of the valence band, which enhances charge carrier transfer from the valence to the conduction band. Poor efficiency in the case of Sb-doped SnS is due to larger mismatch between dopant Sb\(^{+3}\) and host Sn\(^{+2}\), which leads to defects and strain in the crystal.
References