CHAPTER - I

GENERAL INTRODUCTION

"Tin selenide" (SnSe) belongs to the IV-VI group of semiconductors having wide range of practical applications. Bulk and thin films of SnSe and its pseudobinary alloys have great potentialities because of their application in p-n Junctions[1], semiconducting glasses[2], infra-red detectors[3], Hetero-junction solar cells[4], Ovonic type switching devices[5] and photoelectrochemical solar cells[6]. SnSe crystallizes in an orthorhombic structure with space group Pbnm (D_{2h}^{16}) and its unit cell dimensions a = 0.444 nm, b = 1.149 nm and c = 0.415 nm. It has a highly anisotropic structure along the C-axis and it is easy to cleave the crystals along the 'a' and 'b' axes. The phase transition and high temperature structure of SnSe have been reported by many workers[7-11].

Transport properties of SnSe monocrystals have been thoroughly studied[12-17]. Attempts to analyze the electronic properties of this material using only electrical conductivity turned out to be complicated due to the variety of different effects, that may be contributing to the measured values. In order to assist the interpretation of electronic transport phenomena in this system, attempts have been made to use the Hall effect and thermoelectric measurements to separate the contributions due to carrier concentration and mobility[12].

Asanabe[12] has reported that for pure SnSe crystals which have no heat treatment history; the resistivity increases with increasing temperature upto 200°C and then falls via a weak step at about 350°C and the Hall coefficient, being constant in the temperature range from liquid air to room temperature, shows an anomalous hump at 200°C and then falls abruptly via a step at about 350°C similar to that in the resistivity. Annealed antimony-doped specimen has large values of the resistivity and Hall coefficient at low temperatures, but the Hall coefficient decreases abruptly from -70°C and approaches a common curve for pure SnSe specimen. Hashimoto[16] has explained his experimental results on temperature variation of the electrical resistivity and the Hall coefficient of SnSe in the temperature range 2 to 100 K, by assuming that some acceptor levels are generated at high temperatures and are frozen by the quenching, whereas they are annihilated at relatively low annealing temperatures. Umeda[17] has investigated the electrical behaviour of SnSe doped with antimony. He has suggested that the donor levels made by antimony doping are annihilated by the annealing and are generated by the quenching in the same way as the acceptor levels in p-type SnSe. But this explanation is found to be inconsistent because of the fact that mobility of Sb-doped p-type SnSe is decreased by annealing. So to obtain a consistent explanation he has further proposed that there may be simultaneous annihilation or generation of both acceptors and donars. Dang Tran Quan[18,19] recently has studied the influence of grain boundary potential barriers on the resistivity of tin selenide films prepared both by thermal evaporation and solid state reaction.

Photoelectronic and optical properties of SnSe epitaxial films and single crystals have also been studied considerably[20-27], Both direct and indirect transitions have been observed between valance and conduction bands in SnSe bulk samples[20]. The reported values of direct and indirect band gaps are ranging from 1.2 eV to 2.2 eV and 0.8 eV to 0.95 eV respectively. Engelken et al[27] have studied the photoconductance and optical properties of amorphous and polycrystalline films of SnSe, deposited by electro-deposition method. They have observed that the band gap of the material shifts from 0.9 eV to approximately 1.3 eV consistently with the increase of Se:Sn ratio. According to their observation the band gap is indirect. There are many discrepancies in the reported results regarding optical transistions in SnSe bulk material as well as in thin films.

The study of photoconductivity in polycrystalline semiconductor films has a long history which includes an important controversy over the fundamental mechanism. But photoconductivity and long period relaxation in photoconductance SnSe films have received much less attention. Charge carrier photorelaxation time is a basic parameter which can be used to characterize the photoelectric properties of the semiconductor. No such studies on tin selenide films have yet been reported.

In the light of above discussion, this particular research program was undertaken to study some of the structural, electrical, photoelectronic properties and to understand the mechanism of photoconduction and long period photorelaxation in these films of tin selenide, deposited both on glass and mica substrates at various substrate temperatures and having different thickness of the films. The details of these investigations are presented in the subsequent chapters. The program of the work undertaken for the purpose is as follows :-

1. Preparation of the SnSe compound and films, structural characterization of these films by X-ray diffraction, TEM and SEM techniques.

2. Studies on temperature and thickness variation of electrical conductivity and photoconductivity in the temperature range 80 - 301 K, with the aim of probing into the mechanism of photoconduction.

3. Measurements of thermoelectric and Hall effects were carried out to study the temperature variation of carrier concentration, mobility and activation energy in the temperature range 160 - 301 K.

4. Study of the dependence of long period photorelaxation in photoconduction on the oxidation and the temperature of the films.

5. Study of optical properties of SnSe films in the wavelength range 800-1800 nm for obtaining the band gaps and understanding the nature of transitions (direct or indirect).