CHAPTER ONE

GENERAL INTRODUCTION

Indium selenide (InSe) belongs to a group III-VI chalcogenide layer semiconductors, having a wide range of practical applications [1-5]. It is a bidimensional layer piled up with Se-In-In-Se sequence. Each unit layer is bounded to its neighbour by a Van-der-Waal's force. That is why, easy cleavage occurs between the layers. A strong covalent bonding remains within each layer [6,7]. This bonding scheme is the key to the unique property of InSe which is radically different from those of more classical semiconductors as regards their band structure, vibrational spectra, opto-electronic properties and mechanical behaviours. The knowledge of the aforementioned fundamental properties is a prerequisite to the interpretation of photoelectronic behaviour. These properties in layered compounds have been investigated comparatively later than in other semiconductors. The low density of dangling bonds on the surface because of the almost complete chemical bonds within the layer makes it possible to form heterojunction devices with a low interface density of states. The property of intercalation allows to alter the electrical properties of the semiconductors which will be convenient in device processing. But because of mechanical weakness due to week Van-der-Waal's force between layer it is difficult to form the device from layer

semiconductor of InSe. This is overcome by use of epitaxial films of InSe prepared using various methods [8-11]. InSe crystalises in a hexagonal structure with cell parameters a = 4.005 Å and c = 16.640 Å respectively and the space group $P6_3/mmc$. The density is reported to be 5.568 gm/cc [12]. A rhombohedral modification [13,14] is also reported with unit cell parameters as a = 4.0046 Å, c = 25.96 Å space group R3m and density 5.57 gm/cc. There are various reports regarding the synthesis [14,15-18], electron-microscopic analysis [8,11,17,18], electrical and optoelectronic parameters [1,18,19-26], band structure [27-31] etc. In particular, InSe is a material with attractive characteristic for photovoltaic conversions of solar energy. It has an energy gap of about 1.3 eV at room temperature, which is very close to the theoretically predicted one for maximum efficiency in solar cells and a minority carrier diffusion length of about 10 μm which permits efficient current collection. Moreover, InSe is a promising material for applications in electrochemical devices such as solid solution electrode. The large structural anisotropy gives rise to different mobilities of majority carriers, one parallel to the layers and other perpendicular to the layers, owing to the fact that there is almost no overlap of wavefunctions of the separate layers.

The transport properties and the conductivity anisotropy have been studied by several authors [32,33] who had noted a large difference in apparent mobilities μ along the c-axis and in the layer ($\mu_\perp/\mu_\parallel \approx 10^2$). The remarkable photoconductivity behaviours with the occurrence of negative photoconductivity electromemory and photomemory effects have led to propose complex schemes of recombination centres.

The as-deposited films of InSe are amorphous. The disorders and defects (present in the amorphous structure) change due to heat treatment [6,19,34,35]. The diminution of disorders and defects in the structural bonding is known to increase the optical gap according to the model of **Mott** and **Davis** [36]. Radial Distribution analysis technique is applied to determine the basis structure of the material

and the short range order with different thermal treatments. The effect of heat treatment on the optical absorption coefficient, steady state photoconductivity, Hall constants, electrical properties, widths of localised states near the mobility edges etc. are studied. The transformation from amorphous to polycrystalline InSe films under various heat treatments is also studied along with the measurement of the change in Hall mobilities, conductivity etc. The temperature dependence of these parameter is tentatively explained in term of Petriz [37] model where the scattering mechanism is due to a potential barrier introduced by the grain boundaries. But anomalies are found as regards the calculated and observed values of grain size and this may be due to a more complex nature of relation among mobility, grain size and potential barrier than that considered by Petriz. Different authors reported different values of experimental results of the same parameters even following same model of grain boundary scattering mechanism and these may be due to different processes of film preparation.

Both direct and indirect interband transitions are found in the optical absorption spectrum of InSe. The transition in the long wavelength edge is indirect and its value is found to be 1.187 eV at room temperature. The next portion of the spectrum corresponds to direct transition. The direct band gaps are 1.293 eV at room temperature [38]. Optical gaps are determined from optical absorption, photoluminism reflectance etc. by many authors for single crystal, amorphous films and polycrystalline films of InSe with possible variations of the same due to different treatments of the sample. The results vary from one another and there is almost no report of reproducibility of the results.

The phenomenon of long term photorelaxation of residual conductivity with the removal of perturbing sources like light or electric fields is known for long time but no concrete study has been made so far, to evolve a mechanism which can explain such behaviour.

This is extremely important in view of its applicability in the field of photomemory, electromemory, switching devices and solar cell fabrication.

No concrete study has been made to calculate the thermoelectric power either of single crystal or of thin film of InSe. The thermoelectric power is regarded as an important tool for studying the type of carriers involved in conduction and the measurement of carrier concentration for non-degenerate polycrystalline thin films.

In view of the above discussion it is quite certain that a thorough study of the layered semiconductor of InSe is needed both regarding its microstructure and its behaviour. The whole gamut of study can be expressed in lines as follows.

1. Synthesis and single crystal preparation of InSe from spectrally pure indium and selenium.

2. Preparation of both amorphous and polycrystalline thin film adopting various treatments

3. Radial distribution function techniques and XRD line profile analysis techniques (using both variance and Fourier analysis) are used to measure and study grain size, micro-strain, dislocation density, layer disorder, tetrahedral structure, coupling constants, coordination numbers etc.

4. Electrical dark and photoconductivity with temperature variation and to study the mechanism of long term photorelaxation. The different parameters, related to decay of residual conductivity, are measured.

5. Thermoelectric power with temperature variation.

6. Optical absorption graphs and determination of optical band gaps and optical constants.