CHAPTER IX

SUMMARY

A detailed study of the important physical properties such as structural, composition, optical, electrical, thermoelectric, dielectric, breakdown and optical recording characteristics has been carried out systematically on thermally evaporated stoichiometric amorphous and polycrystalline Sb$_2$Se$_3$ thin films. An attempt has also been made to find its suitability as an optical recording storage medium. The important findings are summarised below.

The X-ray diffraction studies of bulk Sb$_2$Se$_3$ reveal its polycrystalline nature. The featureless diffractogram of Sb$_2$Se$_3$ film deposited at $T_S = 303$ K indicates its amorphous nature. The sharp peaks observed for the films deposited with $T_S = 493$ K in the diffractogram confirm its polycrystalline nature. The films have crystalline structure with preferred orientation and growth on some crystallographic planes of which the (240), (231), (130), (120) and (020) were identified. At $T_S = 493$ K, during the nucleation, the atomic orientation of (hk0) planes are found to be predominant.

Scanning electron microscope analysis of surface morphology of the films confirms the results of XRD studies. SEM study reveals that the films deposited at $T_S = 303$ K have a smooth surface, while SEM micrographs of polycrystalline film show grown
microcrystals of different sizes. The high resolution optical microscopic observation has also confirmed the above analysis.

The composition analysis on the thin films of Sb$_2$Se$_3$ using EDAX and RBS techniques reveals the dependence of the composition on the rate of evaporation. The films deposited at the rate of 10 nm/sec are found to possess stoichiometric composition (Sb = 40 ± 2 at %, Se = 60 ± 2 at %). Stoichiometric nature of the deposited films were confirmed by both EDAX and RBS techniques.

The optical parameters such as refractive index (n) and extinction coefficient (k) were determined from transmission and reflection data by solving Heavens equation using Newton-Raphson iterative technique. The refractive index of the polycrystalline films is found to be higher than that of the amorphous films which could be due to some differences in bonding, nearest neighbour distance and to dangling bonds. It is interesting to note that Sb$_2$Se$_3$ thin films are found to exhibit both direct and indirect allowed transition. The indirect allowed transition energies estimated for amorphous (1.2 - 1.3 eV) and polycrystalline (0.9 - 1.1 eV) films of Sb$_2$Se$_3$ are in good agreement with the values reported by earlier workers from other measurements. The direct allowed transition energies found for amorphous (1.5 - 1.7 eV) and polycrystalline (1.0 - 1.4 eV) films are in close agreement with those reported from similar studies. The increased energy gap of amorphous Sb$_2$Se$_3$ thin films over those
crystalline films is supported by the difference existing in the spectral dependence. This suggests that the density of states in the conduction band of the amorphous material is lower or that the matrix elements for optical transitions are suppressed due to the lack of long range order which affect the sensitivity of allowed transitions.

DC conductive measurements reveal the existence of a Poole-Frenkel conduction mechanism in both amorphous and polycrystalline Sb$_2$Se$_3$ films. It is found that the dc conduction in all the samples at high temperatures (300 - 356 K) takes place in the tails of localised states via thermally activated tunneling. An increase in film thickness is found to result in the decrease of activation energy. Anomalous behaviour of electrical conductivity with thickness has been explained on the basis of grain size from SEM pattern. The pre-exponential factor $C$ is also found to decrease during amorphous to crystalline phase transformation, which is attributed to the change in the density of localised states in the band gaps.

The thermoelectric study performed on Sb$_2$Se$_3$ films mainly to determine the type of majority carriers confirmed its p-type nature. Further, the films are found to exhibit linear increase in thermopower with increase in temperature of the hot junction. This is due to the fact that as the gradient increases, creation of electron-hole pair increases and thus there is an increase in the concentration of majority carriers. The increase in thermo-
electric power with thickness is attributed to the reduced grain boundary scattering that results due to the increased crystallised size.

The thickness dependence of dielectric constant in amorphous \( \text{Sb}_2\text{Se}_3 \) films is attributed to the decrease of density of voids with thickness, while in polycrystalline films it is attributed to its grain size variation with thickness. The increase in capacitance in the lower frequency suggests the possibility of an interfacial polarisation mechanism that is prevailing in that region. A frequency-temperature dependence of \( \tan \delta \) reveals a loss peak minima which shifts to higher frequencies with increasing temperature. From Cole-Cole diagrams the spreading factor \( \beta \) and relaxation time \( \tau_a \) have been determined. The frequency dependence of ac conductance of \( \text{Sb}_2\text{Se}_3 \) films at low frequency, indicated the hopping of charge carriers between impurity sites. The ac conductance with temperature is due to the motion of holes in the valence band and to hopping of electrons in the localised states.

The dielectric breakdown studies on chalcogenide \( \text{Sb}_2\text{Se}_3 \) thin films show that the thickness and temperature dependence of the onset breakdown field does not follow the Forlani-Minnaja theory which holds good only for dielectrics.

The optical recording study using beam probe technique reveals very good characteristics of lower thickness \( \text{Sb}_2\text{Se}_3 \) films as an optical data storage medium. Thin films of specific thick-
ness require optimum laser irradiation time with particular power to attain maximum amount of crystallinity starting from amorphous phase. Increase in power density of laser irradiation is found to improve the crystallinity. Increase in scanning speed of the film requires more power to exhibit the same amount of change in transmittance as is attained with low power at low scanning speeds.

The present investigation provides information for the first time on the structural, dc conduction, dielectric, ac conduction and optical recording characteristic of $\text{Sb}_2\text{Se}_3$ thin films.

The diode lasers which provide nanosecond pulses with very low power can be used to study optical recording characteristics in similar lines based on amorphous-crystalline phase transformation, and vice versa to realise this system in an optical recording medium in practice. The fulfillment of this requirement is suggested for further interesting investigations.