CHAPTER - I

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Solid materials can be classified as crystalline or amorphous. The rapidly growing field of solid state physics has already concentrated largely on the crystalline solids than on amorphous one. The study of amorphous semiconductors has become an active field in solid state physics over the last decade. In particular the nature of electronic transport in these materials has attracted much attention during recent years. In order to know electronic transport in amorphous materials, the basic energy band concepts of crystalline solids are discussed in Chapter II. The first concept equally valid for crystalline and for non-crystalline materials is the density of states which we denote by N(E). The density of states in non-crystalline materials does not differ greatly from the corresponding form in the crystalline, except localized states may appear in the forbidden energy range. The wave function is modified in amorphous materials. The mean free path in amorphous materials is large if the deviation of density of state of electron is small and there is absence of axis of symmetry. The mean free path become small if there are strong atomic potential and strong scattering.

Gubanov[1.1] showed that near the edges of conduction or valence band in non-crystalline materials, the states are

localized and the concept of localization plays an important role. The understanding of localization in this case is discussed in Chapter II[1.2]. The extension of localized states to non-crystalline material shows that states exist near the extremities of conduction or valence band. Energy E_c separates the localized states and extended states. This concept was first introduced by Mott[1.3], which is discussed in Chapter II. For energies on one side of E_c, charge transport is due to thermally activated hopping, involving interaction with phonons; so that mobility tends to zero with temperature. For energies on the other side of E_c, diffusion can take place even at the absolute zero of temperature and diffusion coefficient contains no activation energy which is also discussed in Chapter II. This leads to the concept of mobility shoulder. The basic concepts of amorphous semiconductors, such as energy band diagram, band model and band structure are discussed in Chapter II. The band structure determines the electrical transport properties that are commonly measured, such as the electrical conductivity, thermoelectric power and Hall coefficient etc.

The understanding of amorphous semiconductors was not developed until the work of Cohen, Fritzsche and Ovshinsky[1.4]. The research activities of Cohen, Fritzsche, Ovshinsky and others gave impetus to the study of amorphous semiconductors. In order to account for translational disorder, modifications have been proposed in the band

structure of amorphous solids. The well known band models are suggested by Cohen-Fritzsche-Ovshinsky[1.4] and Davis-Mott[1.5]. In contrast to the Cohen-Fritzsche-Ovshinsky and Davis-Mott ideas, a different approach to the under standing of the electrical properties of amorphous semiconductors has been put forward by E_{min}[1.6]. He suggested that the charge carriers in amorphous materials might be small polarons. It is generally accepted that hopping of small polarons is the mechanism responsible for electrical transport in oxide glasses, in which the major constituent is the transition-metal.

Although over the last decade a lot of experimental data is available in the field of transport properties of chalcogenide glasses, the nature of electronic transport still remains unclear in these materials. Several band models have been proposed to explain the electronic structure of these materials[1.5,1.7-1.9]. It has been reported in the literature that, there is a difference between activation energies, calculated from electrical conductivity and thermoelectric power[1.5, 1.10]. In order to reconcile this energy difference, E_{min} and others[1.11-13] proposed that the conduction is by small polaron hopping in extended state below E_v. In order to explain these experimental findings, two mechanisms of quite different physical origin have been proposed. The first interpretation is based on the widely accepted band model of an ideal amorphous semiconductor in which both the

conduction and valence bands are divided into states of localized nature and extended nature. A different approach to the understanding of electrical conduction is based on the assumption that the presence of disorder enhances the probability of small polaron formation.

Several conduction models have been proposed to explain the electrical transport in chalcogenide glasses, largely based on experimental observations of P type materials. Davis and Mott[1.5] proposed a singly activated conduction mechanism in the valence band as :

$$\sigma = C \exp\left(\frac{-E_{\sigma}^{*}}{KT}\right) \qquad \ldots (1.1)$$

where σ is conductivity and E_{σ}^{*} is the conductivity activation energy, 'C' is constant to be in the range of 1 to 1000 Ω^{-1} cm^{-1}. Mott introduced the concept of minimum metallic conductivity given by,

$$\sigma(T) = \sigma_{min}\left(\frac{\nu}{k}\right) \exp\left(\frac{-E_{\sigma}^{*}}{KT}\right) \qquad \ldots (1.2)$$

and thermoelectric power by,

$$S(T) = \pm \frac{k}{e}\left(\frac{E_{S}^{*}}{kT} - \frac{\nu}{k} + A\right) \qquad \ldots (1.3)$$

Here σ_{min} is minimum metallic conductivity. 'A' is heat transport term, ν in the above equation was taken to be

about one half of the temperature coefficient of the optical gap. The above equations 1.1, 1.2, 1.3 are discussed in detail in Chapter III. The results obtained by Nagels - et al.[1.14, 1.15] on the amorphous system with a small addition of silicon gives a nice illustration of these basic experimental facts.

The electrical conductivity and thermoelectric power measurements of Se-Te have been reported by Zope[1.16]. The thermoelectric power in Se-Te is reported by Edmond[1.17] . The field dependence of electrical conductivity of Se-Te has been reported by Mehera[1.18]. However, the d.c. conductivity of chalcogenide glass system, Se-Te-Sb was investigated as function of temperature by P. Nagels and Sakai[1.19, 1.20]. They showed that the conductivity was found to increase with increasing contents of Sb and thus decrease in activation energy. The results of our system, Se-Te-In are discussed in Chapter V on the basis of P. Nagels ideas. On the basis of Overhof and Beyer[2.21] , we have calculated the values of E_Q , $Q(T)$, Q_o, l_1 . They are listed in Table 5.1. The values of E_Q obtained from Overhof and Beyer equation, are in agreement with values reported in Literature[1.13, 1.22].

This view of the electronic properties of amorphous semiconductors will be divided into four main parts. Chapter II describes the basic concepts of amorphous semiconductors such as the energy band diagram of amorphous semiconductors and

various models describing the electronic density of states. Here the fundamental question arises whether the features of the band structure of the crystalline materials are preserved when going from the crystalline to the disordered state. On the basis of these models the different channels for conduction in amorphous semiconductors will be discussed in detail.

Chapter III is concerned with some basic electrical properties of amorphous semiconductors particularly d.c. conductivity and thermoelectric power. An alternative explanation of the transport data of amorphous semiconductors is suggested by E_{min}[1.13].

Chapter IV deals with experimental studies such as preparation of sample, X-ray diffraction pattern, I-V characteristic, d.c. conductivity and thermoelectric power. The experimental observation tables and formulae used for calculations are listed in the same chapter. In this dissertation the results of I-V characteristic, d.c. conductivity and thermoelectric power of bulk samples of amorphous semiconducting Se_{70}-Te_{30}, Se_{70}-Te_{30-x} I_{nx} (where x = 1, 3, 5, 7, 9 % atomic weight) are presented.

The results of above studies are discussed in Chapter V. The X-ray diffraction pattern is studied to know the structure of amorphous material. The non-linear I-V behaviour is discussed on the basis of charge defect states.

The difference of activation energy obtained from conductivity and thermoelectric measurements has been discussed on the basis of long range electrostatic potential fluctuations. The influence of Indium on the electronic transport of amorphous Se-Te is reported on the basis of formation of Indium islands in semiconducting medium.

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