INTRODUCTION

INTRODUCTION

It is no surprise to note that the technological importance of amorphous solids has mushroomed over the past few years. Amorphous semiconductors, with the well-established crystalline foundation as a departure point, offer new frontiers for research and hopefully, promise for technological developments. In the very brief time, we have seen the development of commercial computer memories, television pick-up tubes, solar cells, x-ray mirrors, thermoelectric devices and imaging films based on amorphous materials.

Solid materials can be classified as crystalline or amorphous. The first concept equally valid for crystalline and noncrystalline materials is the density of states which we donote by $g(E)$. The density of states in noncrystalline 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. Amorphous semiconductors are not completely disordered on the atomic scale. Local chemistry provides almost rigorous bond-length, and to a lesser extent, bond angle constraints on the nearest neighbour environment. Unlike amorphous metals, amorphous semiconductors do not consist of close-packed atoms, but

rather they contain covalently bonded atoms. The short range order is directly responsible for observable semiconductor properties such as optical absorption edges and activated electrical conductivities.

The two normal ways of preparing amorphous solids are 1) by evaporation, sputtering, or similar methods of deposition, or 2) by cooling from a melt (quenching). The first method produces thin films and the second bulk material. There must be some structural differences between the same material prepared by different methods, and care is obviously necessary in any comparison of properties.

Generally speaking, most amorphous solids that can be prepared by cooling from the melt are insulators or wide gap semiconductors, in which the mobility gap is greater than about 1 eV. Examples include Se, SeTe, As_2Se_3 and similar chalcogenide compounds or multicomponent systems.

Gubanov [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. This concept was first introduced by Mott[2]. The band structure of amorphous semiconductors determines the electrical transport properties, such as the electrical conductivity, thermoelectric power. The well known band models are suggested by Cohen-Fritzsche-Ovshinsky [3], and Davis-Mott [4]. They all used the concept of localized

states in the band tails. Opinions vary, however, as to the extent of this tailing.

A different approach to the understanding of the electrical properties of amorphous semiconductors has been put forward by Emin [5]. He suggested that the charge carriers in some amorphous materials might be small polarons. He was able to analyze experimental data of dc conductivity, thermopower, and Hall mobility obtained on some chalcogenide glasses. 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.

Chapter 1 places in perspective the various theoretical approaches relating structure of amorphous solids, electronic transport properties in amorphous semiconductors, and origin of magnetic susceplibility in amorphous material.

The section 1.1 deals with new approach to the study of solid state physics, in which periodicity is not considered to be fundamental. Both the conventional and alternative viewpoints are discussed, and the effects of disorder are analyzed. Any problem in solid state theory can be broken down in to three sub problems. The first is that of the equillibrium positions of the atoms constituting the solid i.e., its structure. The structure not only determines the mechanical properties of the material but also

controls the other two sub-problems. One of these is the phonon modes of the solid which determine thermal properties of the material. The other problem is that of the states available to the electrons as they propagate through the solid i.e., the electronic structure. This controls the electrical and optical properties of the material.

The amorphous structure is confirmed from diffraction pattern of an amorphous solid, which consist of broad halos or rings without any evidence of spots. The concept of localized states, mobility edge, Fermi energy are discussed, while describing the structure of amorphous solids. The important problem of electronic structure is the density of states available to electrons as they move through the disordered system, g(E), as a function of their energy E. Once g(E) is known, the near-equillibrium electrical properties of the material as functions of the temperature can be derived from Fermi-Dirac distribution, f(E). Various band models to sort electrical conduction in amorphous semiconductors, are discussed. The nature of defects of chalcogenides, the original proposals of street [6] is discussed in detail. Chemical-bond description given by Kastner et.al [7] is followed by Anderson proposal. This is that in amorphous semiconductors there is a strong tendency for electrons to be paired in bonding configurations, the Coulomb repulsion between electrons at the same site being outweighted by a negative term in the energy due

to electron-phonon interaction which leads to configuration changes in the local atomic structure.

Section 1.2 describes electrical properties of non crystalline semiconductors. Temperature variation of dc conductivity and thermoelectric power is discussed with appropriate mathematical relations. Formulas describing various transport coefficients are presented and are compared with crystalline formulation where appropriate. The essential features of the Davis and Mott model for the band structure of amorphous semiconductors leads to three basically different channels for conduction. Emin's ideas of small polaron formation in non-crystalline material is discussed. Holstein's [8] fundamental concept of "coincidence event", is explained which characterizes the hopping mechanism. The switching mechanism observed in multi-component chalcogenide glasses is discussed.

Section 1-3 describes magnetic properties of materials. The origin of diamagnetism is discussed in detail. Chapter II is concerned with experimental studies such as preparation of sample, X-ray diffraction pattern, I-V characteristics, 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 characteristics, d.c. conductivity, thermoelectric power and magnetic susceptibility of bulk samples of amorphous semiconductors $Se_{70}-Te_{30}$,

Se_{70} -Te_{30-x} In_x (where x = 1,3,5,7,9% atomic weight) are presented. The samples used for experimental perpose are annealed (i.e. heated upto 110°C).

The electrical conductivity and thermoelectric power measurements of Se-Te have been reported by Zope [9]. The thermoelectric power in Se-Te is reported by Edmond [10]. The field dependence of electrical conductivity of Se-Te has been reported by Mehera [11]. The d.c. conductivity of chalcogenide glass ststem, Se-Te-Sb as function of temperature is reported by P. Nagels and Sakai [12,13]. They showed that the conductivity increases with increasing contents of Sb, and thus decrease in activation energy. The results of our system Se-Te-In (after annealing) are discussed in chapter III, on the basis of P. Nagels ideas. On the basis of Overhof and beyer, [14] we have calculated the values of E , Q(T), Q(0), l_1 . They are listed in table 3.1.

Chapter III deals with results and discussion of above mentioned studies. The non-linear I-V behavior 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. Due to annealing the probability of heteronuclear bond formation increases as compaired to homonuclear bonds. It has considerable effect on band gap, which is discussed in

the same chapter. The effect of temperature on diamagnetic susceptibility is discussed.

Although we do not know what new insight will emerge over the next few years, we can be confident that the study of amorphous materials will take its porper place at the forefront of solid state physics in the near future.

REFERENCES

1. Gubanov, A.T. Quantum electron theory of amorphous conductors, consultants Bureau, New York, (1965).

2. Mott, N.F. Advs. Phys. 16, 49 (1957).
   Cohen, M.H. Fritzsche, H, Ovshinsky, S.R. Phy. Rev.

3. Lett. 22, 1065 (1969).

4. Davis, E.A., Mott, N.F., Philos. Mag. 22, 903 (1970).

5. Emin, D. "Aspects of the theory of small polarons in disordered Materials in electronic and structural properties of amorphous semiconductors" Ed. by Comber, P.G., Mort, J. P. 261 (1973).
   (Academic press Lond. New York).

6. R.A. Street, N.F. Mott : Phy. Rev. Lett. 35, 1293 (1975).

7. M. Kastner, H. Fritzsche : Phio. Mag. 37, 199 (1978).

8. T. Holstein : Ann. Phys. (N.Y.) 8, 343 (1959).

9. Zope, J.K., Indian J. Pure and applied Phys. 20, 774 (1982).

10. Edmond, J.T. J. Appl. Phys. 17, 979 (1966).

11. Mehera, R.M., Radheysham, Mathur, P.C., Phys. Rev. B. 19 6525 (1974).

12. Nagels, P., Phys. Status Solidi A 59, 505 (1986).

13. Sakai, H., Shiukawa, K, Inagki, Arizumi Jap, J. Appl. Phys. 13, 500 (1974).

14. Overhof, H., Beyer, W., Phil. Mag. B 49, 19 (1984).