CHAPTER - 1

AN INTRODUCTION TO AMORPHOUS SEMICONDUCTORS AND SELECTION OF THE PROBLEM
1.1 **INTRODUCTION**

The study of amorphous semiconductors has been of considerable interest to scientists as well as engineers from the theoretical and experimental considerations. Experimentalists feel that the properties of multi component amorphous materials will eventually lead to preparation of tailor made materials with suitable changes in their constituents; thus the intrinsic optical properties, namely the optical band gap of amorphous semiconductors can be varied systematically by changing the composition of an alloy system.

Non-crystalline materials have many advantages over their crystalline counterparts as far as their applications are concerned. In general, amorphous solids are relatively easy to prepare. Therefore, large area homogeneous amorphous thin films can be prepared for solar cell or thin-film-transistor applications; bulk glasses can often be readily formed from the melt by relatively slow quenching procedures (or by Sol-gel methods); more importantly near the glass transition temperature the material remains workable (i.e., the viscosity is relatively low) over a range of temperatures so that it can easily be fashioned into various shapes or
drawn into fibres. Furthermore, amorphous materials, particularly bulk glasses, are often structurally homogeneous and isotropic on a macroscopic length scale. As a result, their physical properties are also isotropic and homogeneous unlike crystalline materials which are well known for their anisotropic behaviour. Thus large scale optical transparency is readily achievable in, for instance, silicate glasses used for optical components (including windows) and fibre-optic cables. The absence of structural defects, such as grain boundaries or dislocations make amorphous materials suitable for mechanical engineering applications also.

A number of electronic applications of amorphous materials, almost all of them semiconductors, have been proposed or put into practice, especially after the discovery of doped n-type or p-type amorphous silicon [1]. In many cases, amorphous materials are used simply as passive elements in electronic devices made from conventional crystalline semiconductors. For example, a-SiO$_2$ or a-Si$_3$N$_4$ is used as the insulator layer in various thin film transistor configurations.

Amorphous semiconductors have also been found suitable for electrophotographic applications. The material first used in xerography or document copying machines was a-Se in thin film form (perhaps alloyed with a few % of As to improve the mechanical properties of the films and to reduce
the tendency for crystallization to occur). More recently, a-Si:H films have also been used for this purpose as reported by Shimizu [2].

Perhaps the most important application of the amorphous semiconductors, e.g., a-Si:H is in the direct conversion of sunlight to electrical power. The development of solar cells from amorphous semiconductors has become extremely active nowadays.

Amorphous semiconductors, in particular, Selenium and Selenide alloys exhibit a unique property of reversible structural transformation, which is useful in optical memory devices. Recent research and developments into optical disc memories have been carried out to achieve highly sensitive and stable memories.

Amorphous semiconductors, while forming a single area of study with some unifying ideas, are often divided into two classes - referred to as 'Ge-type' and 'Se-type'. Their distinctions can be made in the following ways:

I Network Flexibility

In accordance with the 8-N rule, the coordination numbers of Ge and Se are, as in the crystalline phases, four and two respectively. Four-fold coordination implies symmetrical bonding and the formation of rigid structures whereas
two-fold coordination is very asymmetrical and therefore has a greater flexibility.

II The Presence of Nonbonding Electrons

In Se, unlike Ge, the uppermost valence band is formed from non-bonding, lone-pair p electrons. These lone-pair orbitals in the amorphous state lose the special orientational relationship present in the crystal and their random arrangement could, in principle, give rise to an extended valence band tail.

Materials that fall into the Ge type class are the tetrahedrally coordinated substances, Ge, Si and III-V compounds. Materials in the Se type class are Se, Te, S and multi-component systems containing a large proportion of a chalcogen element. A mixed system such as $\text{Ge}_x\text{Se}_{1-x}$ can fall into either class depending upon the value of $x$. Nevertheless, the class in which a material falls can be deduced from their properties which are as follows:

a) Paramagnetic Centers

The Ge-type class of materials is characterized by a large density of free spins as evinced by ESR and a Curie-like susceptibility. The density of paramagnetic centers is normally found to lie between $10^{19}$ and $10^{20}$ cm$^{-3}$ and their 'g' factor is close to 2.01. However, a-Si prepared by glow
discharge of silane shows no spin signal; the presence of hydrogen serves to saturate dangling bonds. In contrast to the Ge-type class of materials, Se and chalcogenide glasses, certainly when well annealed, contain no paramagnetic centres or at least a density less than the experimentally detectable limit $\sim 10^{15}$ cm$^{-3}$. Chalcogenide films deposited onto low temperature substrates and maintained at a low temperature [3], however, do exhibit an ESR signal.

b) **Photoinduced ESR**

Although the Se-type class of materials do not normally exhibit ESR signal in the dark equilibrium state, it is possible to photoinduce paramagnetic centers by illuminating with radiation of energy close to that of the band gap at a low temperature [4,5]. The ESR signal associated with such metastable centres has a $g$-value $\sim 2.00$ and corresponds to a density of about $10^{17}$ cm$^{-3}$. The Ge-type class of materials do not exhibit photoinduced ESR, with an exception again being that of hydrogenated silicon.

c) **Luminescence**

Following excitation with radiation in the wavelength range identical to that giving rise to photoinduced ESR, the Se-type class of materials luminesces with varying degrees of efficiency [6]. The radiation is emitted in a band whose
width and position (normally close to half the band gap) can be interpreted in terms of strong electron-phonon coupling. The luminescence is consequently associated with a large stokes shift. On the other hand, luminescence has not been observed in the Ge-type class of materials with an exception to a-Si:H.

d) Variable-Range Hopping Conduction

Particularly at low temperatures, the conductivity of the Ge-type class of materials obey the $T^{-1/4}$ law characteristic of variable range hopping conduction. In contrast, the conductivity of Se and chalcogenides is temperature-activated in an Arrhenius manner with an energy close to one half of the optical band gap.

Apart from the different chemical bonding and physical properties, the above two classes of amorphous semiconductors exhibit some common features which can be summarized as follows:

a) The properties of Amorphous Semiconductors are in general insensitive to the incorporation of impurities: For example, the electrical conductivities of amorphous films of Ge, Si and III-V compounds prepared by vacuum evaporation of the corresponding crystalline phases are independent of whether the starting materials are pure or whether they are doped sufficiently to make the crystals degenerate n or p type. Chalcogenide glasses prepared by
supercooling the liquid are likewise obvious to the presence of several percent of an additional element added to the melt.

b) The Fermi level is found to be pinned near midgap. This feature when considered in respect of impurity incorporation is of course equivalent to (a); if the Fermi level is pinned then doping cannot be achieved.

c) A general similarity of the overall distribution of the density of states in the valence and conduction bands to that in the corresponding crystalline phase.

To explain the above features it becomes necessary to gain an insight into the basic models proposed for amorphous semiconductors which also give an account of the various types of defects responsible for the above mentioned features.

1.2 ELECTRONIC STRUCTURE OF AMORPHOUS SEMICONDUCTORS

The absence of long range order in amorphous semiconductors does not have a major effect on the energy distribution of the electronic levels. Photo-emission studies show that the density of states retains a profile similar to that in crystalline phase and band gaps survive. Of more importance is the presence of short range disorder which manifests itself in the form of band tailing and localization of the electronic states therein. The localized states are separated from the
extended states in both the conduction and valence bands by mobility edges because conduction through the localized states can occur only by a thermally assisted tunneling process which leads to a low (temperature activated) mobility. Even beyond the mobility edges the free carrier mobilities are considerably lower than found in good crystalline semiconductors, owing to strong scattering and a short mean free path. Although some control over the extent of band-tailing is possible, the presence of a continuum of localized levels at the band edges will be considered as an intrinsic property of an amorphous semiconductor.

On the other hand, states deeper in the gap can be classed as extrinsic in the sense that they arise from point defects whose density is a strong function of preparation conditions or post deposition treatments.

To relate the formation of localized states to electrical transport properties, several hypothesis were proposed, which gave rise to different band models. They are as follows:

The CFO model [7], assumes that, in the chalcogenide alloys, the disorder is sufficiently great that the tails of the conduction and valence bands overlap, leading to an appreciable density of states in the middle of the gap. A consequence of band overlapping is that there are states in
the valence band, ordinarily filled that have higher energies than states in the conduction band that are ordinarily unfilled. A redistribution of the electrons must take place, forming filled states in the conduction band tail, which are negatively charged and empty states in the valence band which are positively charged. This model, therefore, ensures self-compensation, and pins the Fermi level close to the middle of the gap. One of the major objections against CFO model was the high transparency of the amorphous chalcogenides below a well defined absorption edge. For a-Si, this model may be more relevant.

According to Davis and Mott [8] the tails of localized states should be rather narrow and should extend a few tenths of an electron volt into the forbidden gap. They proposed furthermore the existence of a band of compensated levels near the middle of the gap, originating from defects in the random newtwork e.g., dangling bonds, vacancies etc. This model was further improved by Mott who suggested that the center band may split into a donor and an acceptor band, which will also pin the Fermi level. At the transition from extended to localized states the mobility drops by several orders of magnitude producing a mobility edge. Indeed, the concept of localized states implies that the mobility is zero at $T = 0 \text{ K}$. The interval between the energies of conduction and valence bands acts as a pseudogap and is defined as the mobility gap.
Cohen [9] proposed a slightly different picture for the energy dependence of the mobility. He suggested that there should not be an abrupt but a continuous drop of the mobility occurring in the extended states just inside the mobility edge. In this intermediate range the mean free path of the carriers becomes of the order of the interatomic spacing, so that the ordinary transport theory based on the Boltzmann equation cannot be used. Cohen described the transport as a Brownian motion in which the carriers are under the influence of continuous scattering.

In recent years experimental evidence, mainly coming from luminescence, photoconductivity and drift mobility has shown that the density of states of a 'real' amorphous semiconductor does not decrease monotonically into the gap but shows many peaks which can be well separated from each other, as in the case of some chalcogenide glasses. The position of the Fermi level is largely determined by the charge distribution in the gap states.

The understanding of the electronic structure of amorphous semiconductors has followed from the postulate that well defined defects are present in these materials [11]. In fact, since some of these defects have a low creation energy, they can be present in concentrations sufficiently large to control the transport behaviour [12]. Of course, the existence of defects in crystalline solids are well known and of great
importance but the constraints of long-range periodicity limit their nature. Freed from the constraints of periodicity, amorphous solids can exhibit a much wider range of defects. By their very nature, amorphous solids are ordinarily metastable, a transition to the lower energy crystalline phase being retarded by a potential barrier which is essentially inaccessible below the glass transition temperature of the material. Local relaxations can take place but crystallization does not occur. The disordered state is quenched by rapid cooling or by direct deposition from a vapor or plasma phase onto a cold substrate. Consequently, the defect structure critically depends on the method of preparation. However, despite the enormous number of defect possibilities, identical preparation conditions do yield reproducible electronic properties and the basic reason for this is the chemical nature of the atoms which constitute the material.

1.3 **DEFECTS IN AMORPHOUS SEMICONDUCTORS**

1.3.1 **Coordination Defects (Positive U)**

In covalently bonded materials with pronounced directional bonding and consequently a well defined local geometry, one type of point defect concerns the atomic coordination. These can be of two types: involving under coordination or over-coordination with respect to the normal coordination of the ideal structure. Under-coordinated defects in covalent
solids are simply dangling, broken or unsatisfied bonds. Over-coordinated defects, though less common, arise when an additional covalent bond is formed datively between a normally coordinated atom and another (utilizing non-bonding lone-pair electrons); the formation of such defects provides the mechanism for producing a negative effective correlation energy for dangling bonds in chalcogenide glasses. A similar type of over-coordinated site has been proposed in a-Si:H, where hydrogen interacts intersitially with long (i.e., weak) Si-Si bonds [13].

The difference between coordination defects in amorphous and crystalline solids is that the isolated defects can occur in non-crystalline state but not in ordered structures.

A simple dangling bond normally contains one electron and is electrically neutral, however, it is amphoteric (being able to donate or accept an electron) and under certain circumstances the electronic occupancy can change, varying concomitantly the charge of the centre. Isolated coordination defects in amorphous covalent materials are labelled in terms of the type of atom that is the site of the defect, together with its coordination number and charge state as subscript and superscript respectively. Thus, for tetrahedrally coordinated materials such as Si or Ge, the different charge states of (under-coordinated) dangling bonds are denoted by \( T_3^0 \), \( T_3^+ \) and \( T_3^- \) (normally bonded atoms are denoted by \( T_4^0 \)).
The energy levels for electron states associated with an isolated dangling bond may be discussed in terms of a simple molecular orbital picture. If we consider the case of a tetrahedral semiconducting material e.g., a-Si, having an atomic electronic configuration \( s^2p^2 \), the atomic levels hybridize to form four \( sp^3 \) molecular hybrids, each of which may admit a bonding or antibonding orbital; solid state interactions then broaden the molecular levels into bands separated by a band gap (Fig. 1.1). A dangling bond, or non-bonding orbital, containing a single electron will therefore have an energy level lying at the zero energy for the \( sp^3 \) hybrids, viz near the middle of the gap (if atomic relaxations are neglected). Thus structural defects such as dangling bonds are expected to electron states deep into the gap; the precise position of the energy levels, however, will depend crucially on factors such as structural relaxation around the defect or the electronic character of the states at the top of the valence band and the bottom of the conduction band from which the eigen function of the defect state derives.

The density of states in the gap for an amorphous semiconductor containing dangling bonds has been depicted in Fig. 1.2. The left mid-gap band in this figure corresponds to the neutral dangling bond containing a single electron (spin) and is 'donor-like' (i.e. neutral when occupied) and the right mid-band gap corresponds to a different charge state of the same defect, namely when an extra electron is placed
Fig. 1.1
Localised States

$N(E)$

$E_V \quad E_F \quad E_C$

Fig.12

Defect states
in it and is 'acceptor-like' (i.e., neutral when empty). Under normal circumstances, the net energy cost for this addition is positive, it costs an extra energy (the Hubbard or correlation energy):

\[ U = \langle \frac{e^2}{4\pi\epsilon_0\epsilon R_{12}} \rangle \]

where \( R_{12} \) represents the appropriate separation for two electron at the same site and a configurational average has been taken in evaluating \( U \).

The materials which come closest to realizing the modified Davis-Mott model are probably evaporated or sputtered a-Si or Ge films. These amorphous thin films exhibit a large ESR (\( \sim 10^{19} - 10^{20} \) spins cm\(^{-3}\)) in their as prepared state and a concomitant high density of states in the gap which naturally explains the observation that they cannot be doped.

This is not the case for hydrogenated a-Si:H alloys, prepared for example by glow - discharge decomposition of silane, which have a low residual density of gap states that the subsitutional introduction of P, As or B can easily dope the materials n- or p-type [1]. Presumably, the presence of the hydrogen acts in the main part to satisfy any dangling bonds, thereby removing the defect states in the gap, repla­
ing them with Si-H bonding states deep in the valence band and rendering the material dopable.
1.3.2 Coordination Defects (negative \( U \))

Although the isolated dangling bond is a possible entity in a covalent random network structure, if dangling bonds occur at voids or other internal surfaces, they can reconstruct so as to lower the total energy, thereby changing the electron occupancy and hence the charge state of the defects.

The essential features of the 'charged dangling bond' model may be understood by consideration of the monatomic system, amorphous Se, illustrated in Fig. 1.3. The structure of amorphous Se, which is two fold coordinated is believed to consist mainly of chains (with perhaps a few rings). Any chain end will be the site of a dangling bond orbital, which in the simplest case will contain an unpaired electron and be electrically neutral relative to the bulk; this dangling bond defect can be written as \( D^0 \), in Mott's model [14] or equivalently \( C^0_1 \), referred to Kastner's model [12]. Mott et al. [14] postulated that, following Anderson [15], electrons residing at \( D^0 \) centres should experience a negative \( U_{\text{eff}} \) and electron pairing should be energetically favourable as a result of atomic rearrangements. Electron-lattice coupling is strong in amorphous chalcogenide because of the low atomic coordination resulting in a high degree of network flexibility, but more importantly, there exist non-bonding, lone-pair \( \pi \) orbitals at the chalcogen atoms which may be utilized in forming additional bonds, and which are
Fig. 1, 3
energetically accessible since they are high lying, forming
the top of the valence band [16]. The transfer of an electron
from one D⁰ (C¹) centre to another produces one site which
has the original dangling bond orbital containing two spin
paired electrons and which is consequently negatively charged
(D⁻ or C⁻) and the other which has an empty orbital which is
then free to form a dative bond with the lone-pair of a fully
connected neighbouring atom; the defect now becomes threefold
coordinated and positively charged (D⁺ or C⁺₃), as shown in
Fig. 1.3(a). In the latter case the site of the defect moves
from the originally dangling bond to the atom providing lone-
pair electrons for the dative bond which correspondingly
becomes over-coordinated. The repulsive Hubbard energy U
involved in placing an extra electron on the same site to
form a D⁻ centre is postulated to be out weighed by the
energy gained in forming the extra bond at the D⁺ site,
rendering the reaction

\[ 2D^0 \rightarrow D^+ + D^- \]  \tag{1.1}  

exothermic with an overall negative effective correlation
energy (Fig. 1.3(b)). This process can be illustrated in terms
of a configurational coordinate diagram (Fig. 1.3(b)). The
appropriate configurational coordinate q in this case may
be taken to be the sum of the distances between two D⁰ centres
and their respective nearest neighbour, but non-directly
bonded atoms $q_1 + q_2$. Transfer of an electron between $D^0$ centres without a change in configuration costs the Hubbard energy $U$, but the lowest energy state for the two resulting oppositely charged centres lies at a different configurational coordinate because of the atomic relaxation (bonding) that takes place at the $D^+$ centre; the energy for this equilibrium configuration is lower by $U_{\text{eff}}$ than that for the two $D^0$ centres.

There are in fact two possible configurations for the neutral defect $D^0$ in chalcogenide glasses, one being under-coordinated ($C_1^0$) and the other over-coordinated ($C_3^0$). Kastner et al. [12] proposed that the symmetric $C_3^0$ centre has the lowest total energy, whereas Mott et al. [14] believed that the actual configuration lay between the two, with one elongated bond.

The charged defects $C_3^+$ and $C_1^-$ have been called by Kastner a valence-alternation pair (VAP), since the various under and over-coordinated sites can be considered as different charge states of the same defect. In compound chalcogenide glasses, $U_{\text{eff}}$ is expected to be negative, since the formation of a valence-alternation pair (VAP), $C_3^+$ and $C_1^-$, from two normally bonded $C_2^0$ atoms via the reaction

$$2C_2^0 \rightarrow C_3^+ + C_1^-$$

involves essentially just a bond flip, conserving the total
number of bonds and therefore the VAP creation energy $E_{\text{VAP}}$ might also be expected to be low [12]. Consequently, a relatively high density of coordination defects (charged in the case of compound materials) should be present in thermal equilibrium in chalcogenide melts, which will be frozen-in on quenching to form a glass, with a concentration depending on the temperature at which equilibrium was last established, namely the glass transition $T_g$. Thus the concentration of randomly distributed VAP defect centres may be given by

$$n_R \sim n_o \exp \left( - \frac{E_{\text{VAP}}}{2k T_g} \right) \quad (1.2)$$

where $n_o$ is the total (chalcogen) atomic density. Since the VAP centres $C_3^+$ and $C_1^-$ are equally and oppositely charged, there is a tendency for them to pair up in the melt under the action of their mutual coulomb interaction, thereby lowering the creation energy even further; the concentration $n_1$ of such 'intimate-valence alternation pairs'--IVAPs [14] would therefore be higher than $n_R$. It may be mentioned that VAPs pin the Fermi energy, IVAPs do not; the concentration of VAPs is expected to be far more sensitive than that of IVAPs to the addition of dopants that form charged centres. Luminescence could in principle arise from either VAPs or IVAPs.

1.4 METHODS FOR THE DETERMINATION OF THE DENSITY OF DEFECT STATES

For amorphous semiconductors physical properties,
generally optical and electrical, are determined by the
defect states and therefore it can in turn be used as bases
for experimental probes of the defects themselves. The
defect population is often the limiting factor in determining
the electronic performance of an amorphous semiconductor. The
techniques to be discussed below, for determining the density
of localized states are generally applicable to all amorphous
semiconducting (insulating) materials, i.e., optical absorption,
whilst others, notably the junction techniques require the
amorphous material to have such a low background density of
states in the gap that the Fermi level can be moved freely
relative to the band edges, which restricts the applicability
of such techniques essentially to a-Si:H.

1.4.1 Junction-related Spectroscopies

A number of techniques that have been developed to
investigate the density of localized states (DOS) in the gap
region of amorphous semiconductors exploit the fact that band
bending can occur at an interface between the semiconductor
and some other material and the magnitude of these junction
related effects is determined by the DOS. These techniques
such as field effect methods, various capacitance related
methods and deep level transient spectroscopy (DLTS) have
all been used in this way, particularly in the study of
a-Si:H [17].
Such techniques can be divided into three categories. Field-effect and capacitance voltage (C-V) measurements essentially probe the space-charge region at the interface under steady-state conditions, and information on the DOS is obtained by repeating the measurement at a number of applied voltages. The other techniques involve dynamic measurements, in which the capacitance is measured as a function of frequency or temperature, which therefore set the time or energy scale on which the space-charge is probed; the DOS is determined by varying the band bending while keeping the space-charge distribution essentially static. The DLTS technique involves a substantial change in the properties of the interface region by (optical) perturbation of the gap states to give a non-equilibrium occupancy; during the recovery process the capacitance or current is measured, the time or temperature dependence of which is used to give an estimate for \( N(E) \). This category also includes techniques such as thermally stimulated current (TSC) or capacitance (TSCAP) methods.

1.4.2 Field-effect Method

The field effect method gave historically the first evidence that the density of gap states in a-Si:H was much lower than in a-Si [18]. In this method Fermi level is moved by application of a high electric field through a gate insulator. The resulting change in the conductivity of the material, measured using two ohmic contacts, is interpreted to
obtain the DOS in the mobility gap. However, this method is subjected to many potential problems. This method assumes that no charge is trapped at the interface (or in the bulk of the material) being studied, and since a region extending typically only 20-100 Å from the interface surface is probed, the field-effect method is an extremely surface sensitive technique. As a result, inhomogeneities and charge trapping centres at the interface between semiconductor and insulator can affect the results obtained. Also the method is rather insensitive to fine details, such as the presence of peaks in the DOS profile. Therefore, the field-effect method is not capable of detecting fine scale features, such as peaks corresponding to defect levels in the DOS deep within the gap of amorphous semiconductors.

1.4.3 Steady State Capacitance Measurements

In the (C-V) method, \( N(E) \) is obtained from the steady state capacitance voltage characteristics of an a-Si:H metal oxide-semiconductor (MOS) structure [19], Schottky barrier [19-22] or p-n junction [23]. In the limit where the frequency is low enough to allow midgap states to follow the oscillating voltage, used for capacitance measurements, it is straightforward to obtain \( N(E) \) from the C-V data, provided interface states can be neglected. Unfortunately, this is precisely the set of conditions (low frequency and/or high temperature) where the anomalous effects due to interface states have been reported [20,24].
Recently, a number of studies have inferred \( N(E) \) at midgap from the frequency and/or temperature dependence of the capacitance of an a-Si:H Schottky barrier \([20, 21, 24-26]\). These sort of measurements have an advantage as they may be made in a regime of temperature and frequency which is less sensitive to interface states than C-V and field-effect measurements \([20-22,24]\). Several important results have been obtained by such measurements. Viktorovitch \([24]\) has shown that the bulk \( N(E) \) at midgap depends strongly on sample preparation conditions and that the interface state density may be very large in MOS structures. Such techniques have an inherent shortcoming, however, in that they are able to measure \( N(E) \) only over a relatively small portion of the gap near Fermi level. Furthermore, the identification of bulk and surface contributions to the signal is not always straightforward.

1.4.4 Isothermal Capacitance Transient Spectroscopy (ICTS)

The isothermal capacitance transient spectroscopy (ICTS) using a voltage or a light pulse has been developed and used by Okushi et al. \([27,28]\) for finding DOS in a-Si:H. In voltage pulse filling, a reverse bias is applied across the diode to perturb the occupancy of states. However, it produces the transient corresponding to the majority carrier traps only. In n-type material, for instance, this corresponds to electron emission from the states in the upper half of the
gap. In order to create a metastable initial condition for the minority carrier traps (hole traps in n-type material), one can introduce mobile minority carriers by shining band gap light on the sample. Light generates electron hole pairs which are subsequently trapped, thus perturbing the gap states occupation in the lower half of the gap. The emptying of the traps with time, after either perturbation, changes the junction capacitance which when measured as a function of time at a constant temperature, produces an ICTS signal. Since, it is a transient measurement, ICTS is insensitive to surface states. The transient measurements probe the same physical parameters as does the steady state method. The choice between the steady state and transient measurement mode is ultimately related to the case of data analysis or insensitivity to extraneous effects such as interface states.

1.4.5 Deep Level Transient Spectroscopy

Lang et al. [29] have used deep level transient spectroscopy (DLTS) to obtain the DOS in doped a-Si:H. In this technique, the difference in capacitance of a Schottky diode or p-n junction is measured, at two suitable time intervals, after excitation with a light or voltage pulse, as the temperature is continuously raised [30]. This gives the dynamic response of the junction space charge region. A DLTS spectrum consists of a series of measurements of capacitance transients following voltage pulses as a function of
temperature to probe the energy dependence of the DOS distribution.

The (capacitance) DLTS technique has the advantage that it is rather insensitive to surface states at the semiconductor interface. However, it has the disadvantage since it is limited to doped (highly conducting) samples because of constraints imposed by dielectric relaxation time.

1.4.6 Photoluminescence

It must be stressed at the outset that the phenomenon of luminescence is not solely associated with the presence of structural defects, that luminescence can result from intraionic electronic transitions of transition metal (3d) or rare earth (4f) atoms in amorphous matrices. However, photoluminescence is also observed in many amorphous materials which do not contain such luminescent impurities, and therefore the phenomenon must also have a more general origin. Band-to-band photoluminescence could occur, electron hole pairs (excitons) created optically by photons having energies comparable to the band gap would then recombine radiatively directly emitting a photon of energy also comparable to the band gap. Often, however, photoluminescence spectra are observed at energies considerably lower than the energy of the exciting photons, and electron states in the gap are often involved. These states can be band tail states, but
are more often associated with structural defects (dangling bonds). Moreover the deeper into the gap a level lies, the stronger will be the electron-phonon coupling and this will greatly influence the luminescence process. The DOS is then deduced from photoluminescence spectra, as in the chalcogenide glass $\text{As}_2\text{Se}_3$ [31].

1.4.7 Thermally Stimulated Currents

In this method, the traps in semiconductors are filled by excitation (by light or a high electric field) at a low temperature and then the excitation is put off. If the temperature is low enough the carriers remain trapped even in the absence of excitation. The temperature of the semiconductor is then raised at a constant rate and as a result the carriers are freed. The liberated carriers contribute to an excess conductivity, measured as an excess current in the presence of an electric field. This excess current when measured as a function of temperature during heating is known as a TSC curve. A single trap level in the semiconductor shows a peak in the TSC curve at a temperature which depends upon the energy of the trap level, capture cross-sections of the traps and the heating rate. By making suitable assumptions about trapping kinetics, the position of trap level and its capture cross sections can be determined by varying the heating rate [32,33,34]. If there is a discrete distribution of traps in the material, the TSC may show several peaks or
a structure corresponding to the distribution of trap depths.

1.4.8 **Space Charge Limited Currents**

This technique has been used to study the electronic density of states (DOS) continuously distributed in the gap of insulating thin film materials [35-37]. In this method, the I-V characteristics of the sample are measured in the high-electric-field region. These non-ohmic characteristics are influenced by the traps in the material and can be used to calculate the DOS. The method has been applied to obtain the DOS in a-Si:H using samples with ohmic contacts [38-40] as well as Schottky diodes in high forward bias region [41]. The results were similar. This method has the advantage that it is not influenced by surface states. But here, one assumes that the material is homogeneous and that the DOS does not change from place to place. Some other measurements, from which DOS has been deduced are photoconductivity decay [42], electron spin resonance [43] and optical absorption [44], transient current spectroscopy [45], transient voltage spectroscopy [46] etc.

1.5 **SELECTION OF THE PROBLEM**

The emergence in recent years of amorphous semiconductors with potential theoretical and practical importance [47] has given a great stimulus to studies of basic properties of these materials. Defects play a vital role in case of
semiconductors as their electronic properties are particularly sensitive to the presence of defects and some of these properties are sometimes a direct consequence of this presence. The vast utilization of semiconductors in modern electronics demands an extensive study on the nature of defects present in these semiconducting materials.

Research on amorphous Si has developed rapidly in recent years. This has been particularly stimulated by the discovery of an existence of valence controllability in hydrogen passivated amorphous Si. This material, owing to a low density of states in the band gap, can easily be doped and offers a new electronic device material. By contrast, electrical conduction in chalcogenide glasses is still hard to control by impurities, it remains almost intrinsic in these glassy semiconductors [47]. Most of the chalcogenides show p-type conduction. Since the concentration of intrinsic defects is very high in case of chalcogenide glasses, a large amount of impurity atoms are needed to exceed the intrinsic defect states. In most of the cases, the high impurity concentration brings the material out of glass forming region. This behaviour generally seems to hold good for bulk chalcogenide glasses. However, there have been reports that glasses of the Ge-Se, Ge-Se-Te and Ge-S systems exhibit p→n transition when doped with high concentrations of Bi and Pb [48-56]. The reason for the appearance of n-type conduction
is still not clear. But, no doubt, the above reports have provided a breakthrough that doping can be achieved in these glassy semiconductors. Since these glasses do not have fixed material parameters, so their material parameters can be varied by changing composition and fabrication conditions. A number of materials can therefore be investigated with emphasis on reducing the density of localised states.

To measure DOS in amorphous semiconductors different methods can be used with all their advantages and their limitations, as has already been discussed in the previous section. However, for chalcogenide glasses, because of the difficulty in forming p-n junctions, techniques such as junction spectroscopies could not be used for DOS determination. Also TSC measurements done on chalcogenide glasses did not yield much information [57,58]. This is mainly because the carriers in the chalcogenide glasses have usually small drift range and that their drift mobility is small [59,60]. Nevertheless, some experimental data on DOS determination is available which has been summarised in Table 1.1.

A glance at Table 1.1 shows a discrepancy between the values of DOS obtained by different measurement techniques, on the same material. To explain this discrepancy, it is necessary to consider several factors. One factor is the possibility of differences in bulk properties of films when one compares samples deposited at different times in a given
### TABLE - 1.1

<table>
<thead>
<tr>
<th>Amorphous Material</th>
<th>Type of Measurement</th>
<th>Density of Defect States (cm(^{-3}) eV(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(_2)Se(_3)</td>
<td>a.c. conductivity</td>
<td>(10^{18})</td>
<td>61</td>
</tr>
<tr>
<td>As(_2)Se(_3)</td>
<td>Photoluminescence</td>
<td>(10^{16}) to (10^{18})</td>
<td>62</td>
</tr>
<tr>
<td>As(_2)Se(_3)</td>
<td>Optical absorption</td>
<td>(2.0 \times 10^{18})</td>
<td>63</td>
</tr>
<tr>
<td>As(_2)Se(_3)</td>
<td>Current-voltage characteristics</td>
<td>(3.0 \times 10^{15})</td>
<td>64</td>
</tr>
<tr>
<td>As(_2)S(_3)</td>
<td>a.c. conductivity</td>
<td>(5.0 \times 10^{17})</td>
<td>61</td>
</tr>
<tr>
<td>As(_2)S(_3)</td>
<td>Photoluminescence</td>
<td>(10^{17})</td>
<td>62</td>
</tr>
<tr>
<td>As(_2)S(_3)</td>
<td>Optical absorption</td>
<td>(2.0 \times 10^{18})</td>
<td>63</td>
</tr>
<tr>
<td>As(_2)Te(_3)</td>
<td>Photoconductivity decay</td>
<td>(3.0 \times 10^{19})</td>
<td>65</td>
</tr>
<tr>
<td>As(_2)Te(_3)</td>
<td>a.c. conductivity</td>
<td>(3.0 \times 10^{19})</td>
<td>66</td>
</tr>
<tr>
<td>Ge(_4)Se(_5)Te</td>
<td>Current-voltage</td>
<td>(2.0 \times 10^{18})</td>
<td>67</td>
</tr>
<tr>
<td>Ge(_4)Se(_5)Te</td>
<td>Current-voltage</td>
<td>(5.0 \times 10^{16})</td>
<td>68</td>
</tr>
<tr>
<td>Sb(_2)S(_3)</td>
<td>Current-voltage</td>
<td>(3.5 \times 10^{14})</td>
<td>69</td>
</tr>
<tr>
<td>Sb(_2)Se(_3)</td>
<td>Current-voltage characteristics</td>
<td>(3.5 \times 10^{16})</td>
<td>64</td>
</tr>
<tr>
<td>Te(<em>{53})As(</em>{32})Si(_{10})Ge(_5)</td>
<td>a.c. conductivity</td>
<td>(4.5 \times 10^{19})</td>
<td>66</td>
</tr>
<tr>
<td>Te(<em>{1.5})As(</em>{2})Se(_{1.5})</td>
<td>Photoluminescence</td>
<td>(10^{16}) to (10^{18})</td>
<td>62</td>
</tr>
<tr>
<td>Wide Variety of chalcogenides</td>
<td>Electron spin resonance</td>
<td>(10^{14})</td>
<td>70</td>
</tr>
</tbody>
</table>
deposition system. In order to properly compare the different DOS experiments it is much preferable that all the samples be co-deposited. Obviously, undue stress should not be placed on differences between the values of N(E) obtained by different techniques in different laboratories. The best comparison between DOS techniques would involve different measurements of films on the same substrate.

Another factor here is the variations in sensitivity of different DOS measurement techniques to the spatial distributions of gap state density. In particular, it is essential to distinguish between a bulk DOS and film interface states at both the top and bottom surfaces. Although theoretically the sensitivity of SCLC to interface states is negligible, it can and must be tested in the way SCLC scales with film thickness. All the thickness scaling evidence[71-74] indicate that SCLC is a bulk effect.

The dependence of current on applied voltage resulting from injection of carriers into amorphous Se has been studied by various authors [75-79]. The results obtained showed that for small voltages ohmic conduction is obtained but for high voltages a non-linear dependence is observed. The currents in this region have been interpreted as space-charge limited currents due to the presence of trap levels in the forbidden band. The existing data may be summarized as follows:
\[ j = AV \exp (BV) \] [Hortk, 76], Uniform distribution of trap levels

\[ j \propto v^{3.8} \] [Lanyon, 77], exponential distribution of trap levels

\[ j \propto v^2/d^3 \] [Viskakas, 78], single trap level

where 'j' is the current density and 'd' film thickness.

The experimental data obtained by these authors cannot be correlated with a single functional dependence. The discrepancy might lie with the assumptions made in the SCLC analysis.

Thus, much is to be done to find an answer to these controversies so that in future the various DOS tools can be reconciled and a consistent picture of \( N(E) \) throughout the gap in various chalcogenide glasses can be achieved. Problems yet to be solved are the basic parameters affecting the density of states \( N(E) \) and its energy distribution in the mobility gap. The present work is an attempt to provide some important conclusions in this direction through a systematic investigation of DOS using SCLC technique and a.c. conductivity. SCLC has been chosen since it is relatively simple to measure and can potentially yield bulk DOS near Fermi level.
The physical properties of glassy $\text{Ge}_x\text{Se}_{1-x}$ system have been studied by various workers in past. Street and Biegelson [80], Shirafuji et al. [81], Koos and Somogyi [82] studied the photoluminescence in $\text{Ge}_x\text{Se}_{1-x}$ system and found these properties to be composition dependent. Various other physical properties such as drift mobilities [83], photocontraction [84], photoconductivity [85] and elastic properties [86] have been carried out in various laboratories. These properties have also been found to be composition dependent. It is also reported by above workers that a sharp transition in the physical properties occurs at a particular value of $x$ indicating a change in the bonding arrangement at higher concentration of Ge in $\text{Ge}_x\text{Se}_{1-x}$ system. It is, therefore, interesting to make a study of DOS determination as a function of Ge concentration.

Recently, it has also been pointed out that Se-Te [87] alloys have some extra advantages over amorphous Se as far as their use in xerography is concerned. Se-Te alloys are widely used firstly because they have a higher photosensitivity than pure Se and secondly because Se-Te alloys are harder than pure Se. The structural studies and various physical properties of these alloys, e.g., photoconductivity and optical absorption have been studied in various laboratories. It is found that with increasing Te concentration
the band gap decreases [88]. Schottmiller et al. [89] have studied the effect of addition of various elements (S, Te, Bi, As, Ge) on the structure of glassy Se by Infra-red and Raman spectroscopy. The Raman spectra measurements of various Se-Te alloys near pure Se [90] had indicated that tellurium enters as co-polymer chains and tends to reduce the number of Se₈ rings. Kotkata and El-Mousley [91] have also reported that in elemental Se, each atom must have two neighbours to satisfy the valence requirement. This is achieved either by formation of small molecules Se₈ or linear polymeric chains Seₙ and addition of Te forming bonds with Se.

From the above discussion, it is clear that Se-Te and Ge-Se alloys are of considerable interest for the study of DOS distribution. With this object in mind, the author proposed to deal with two systems (a) Se-Te based alloys (b) Ge-Se based alloys.

Chapter 2 deals with the high field conduction in binary chalcogenide glasses and chapter 3 with ternary chalcogenide glasses with a specific aim to identify the process
responsible for non-ohmic behaviour at high fields in these glasses. It is established that space charge limited conduction is responsible for the observed non-ohmic behaviour at high fields. The density of defect states has also been estimated for various binary and ternary chalcogenide glassy alloys and the composition dependence is discussed.

Chapter 4 of the thesis reports the a.c. conductivity measurements in some binary and ternary chalcogenide glasses as a function of temperature and frequency. It is shown that Bipolaron hopping conduction theory does not successfully explain the temperature dependence of a.c. conductivity at high temperatures. However, the theoretically calculated values of a.c. conductivity using single polaron hopping conduction theory matches with the experimental values obtained in the present glasses. The density of defect states has also been calculated using the above measurements.