

**OPTICAL PROPERTIES AND ELECTRICAL
CONDUCTION MECHANISMS OF ELECTRON
BEAM EVAPORATED Cu-GeO₂ THIN CERMET
FILMS**

A thesis submitted for the degree of Doctor of Philosophy

by

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To

Fowzia, Tuhin and Adnan

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Preface

The main goal behind this research work was to study the electrical conduction mechanisms in Cu-GeO₂ thin cermet films in the dielectric regime. The results from a large number of experiments on optical absorption, DC conductivity, Hall effect and AC conductivity studies were combined together to provide the basis of a comprehensive understanding of the electronic transport properties in this material.

Chapter 1 reviews critically the past and present advances in the theoretical and experimental studies of the transport properties in amorphous semiconductors. In particular, this chapter provides an extensive survey of optical properties, various models of AC and DC conduction mechanism and examines the origin of Hall effects in amorphous semiconducting materials. It becomes clear from this survey that although striking progress has been made in the knowledge of electronic transport mechanisms, there are many aspects which remain unresolved and require further investigation.

Chapter 2 deals with various film deposition and thickness measurement techniques which are commonly used in the preparation of amorphous thin films. In particular, this chapter contains a brief description of the evaporation system and the electron beam evaporation technique utilized for preparing Cu-GeO₂ thin films.

Chapter 3 contains the results of all optical measurements performed on the films of various thicknesses and compositions. It begins with a brief introduction, followed by different sections explaining the theoretical models, experimental procedures, results and discussions.

Chapter 4 is devoted to the study of DC conductivity in two and four probe planar configurations. The results are analysed in terms of various conduction and band models. This chapter also briefly describes various equipment used in the study together with experimental limitations and difficulties one encounters while making measurements on high-resistivity materials.

The utilization of the Hall effect has been a longstanding tool in the study of electrical transport mechanism in semiconductors. It provides directly the information about charge carriers thermally excited from the impurity atoms. Combining this information with DC conductivity measurements yields the mobility of the carriers. Temperature dependence of Hall mobility in conjunction with temperature dependence of DC conductivity yields valuable information about the conduction mechanism. In high resistivity materials, detecting a Hall signal is an extremely difficult task. It is often overshadowed by relatively large background signals. As a result sensitive detection techniques are required. All these form the subject of **Chapter 5**.

Transport properties determined from the combined knowledge of optical, DC conductivity and Hall effect results do not provide comprehensive information about the influence of defect states associated with structural irregularities and discontinuities in the material. AC loss measurements are dominated by such defects and, therefore, information about these states can be obtained from a complete understanding of the AC conduction mechanism. These provide the subject of **Chapter 6**.

Chapter 7 contains summary and shortcomings of the present work and suggests further research in this field.

Finally, we take liberty in mentioning that parts of this work were reported in the following papers:

A.M.Al-Saie, M.H.Rahman and J.Beynon

"Optical properties of Cu-GeO₂ thin cermet films"

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"Electrical conductivity and Hall effect in Cu-GeO₂ thin cermet films"

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"AC electrical conduction mechanism in electron beam evaporated Cu-GeO₂ thin cermet films"

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Abstract

Optical, DC, and Hall effect measurements were performed on a number of electron beam evaporated Cu-GeO₂ thin cermet films with the aim of obtaining information about the DC conduction mechanism. Optical absorption studies showed that incorporation of Cu in the matrix of GeO₂ introduces defect states leading to a reduction in the optical energy gap. It was found that the optical energy gap increases with increasing film thickness but decreases with increasing copper concentration. The DC conductivity results revealed that above a certain temperature T_C (i.e 355 K, 367 K and 375 K for 30, 20 and 5 at.wt.% Cu films, respectively) conductivity increased sharply with activation energy lying in the range 0.66 to 0.77 eV. Below T_C , conductivity is weakly activated with activation energy lying in the range 0.10 to 0.25 eV. Hall effect experiment was performed to investigate the sharp transition points in the DC conductivity curves. A sign reversal in Hall mobility was observed for all the samples. Furthermore, the Hall mobility showed a maximum at a critical temperature (T_C) identical to that of the DC conductivity. A detailed analysis of these results showed that the DC conductivity was dominated by a mixed conduction process and that the small polaron model best describes the conduction mechanism. Below T_C , the conductivity is identified with hopping of carriers through localized states. Above T_C , carrier concentration is believed to govern the conductivity. From the combined knowledge of optical absorption, DC conductivity and Hall effect results a room-temperature band diagram (for 30 at.wt.% Cu films) is proposed in which the mobility gap is calculated to be 3.78 eV. Above T_C , the mobility gap reduces to 2.62 eV.

The AC conductivity and dielectric loss showed striking minima around a cut-off frequency ($\approx 10^5$ Hz) indicating

two fundamentally different dielectric processes in operation. Below 10^5 Hz, the small polaron tunneling model best describes the conduction mechanism. Above 10^5 Hz, the conductivity showed a quadratic frequency dependent behaviour in agreement with Mott-Davis type photon-activated resonant processes. These results further imply that the AC conductivity can not be described by a single universal power-law. Instead, a two power-law hypothesis is advanced.

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INTRODUCTION

For many years there have been extensive studies of ceramic-metal (cermet or granular metal) thin films because of their potential applications in electronics industries [Neugebauer et al. 1962, Milgram et al. 1966, Coutts 1969, Hill 1969, Morris 1972, Sheng 1972; 1992, Abeles et al. 1975, Ritter 1975, Morris et al. 1977, Hill et al. 1977, Song et al. 1989, Steele et al. 1992, Al-Saie et al. 1993, Rahman et al. 1994]. The excellent transmittance (about 85-92%) of the cermets in the visible region and continuous variation of the absorption coefficient, refractive index and extinction coefficient as a function of photon energy make them ideal as optical devices [Tauc et al. 1966, Davis et al. 1970, Daham et al. 1990]. These effects form the basis of such devices as photoelectric devices, absorption filters, solar cells, coating of all kinds such as dielectric mirrors and antireflection coatings; optical imaging equipment such as telescopes, binoculars, microscopes and cameras; and information storage devices such as computers [Chopra 1969, Maissel 1970, Moridi et al. 1977, Pulker 1984, Ohring 1992].

One of the challenging aspects of the thin film amorphous semiconductors is the possibility of controlling short-range order parameter and thereby achieving a drastic change in the physical properties of these materials. A large variety of optoelectronics and microelectronics devices result from the fact that almost any physical property depends strongly on the thickness, composition and structural state of the material. Depending on the metal content, a cermet film can have widely varying resistivity, temperature coefficient of resistivity (TCR)

and thermopower. Consequently, this material has found numerous and varied applications in microelectronics industries. These include resistors, capacitors and inductors; electromechanical sensors; heating elements; memory and switching devices; thermoelectric conversion elements and thin film magnetic heads [Nava et al. 1984, Ohring 1992]. Furthermore, since a large number of properties of these films undergo rapid changes with temperature, such materials can be used for a variety of thermal devices such as thermal detectors, thermometers and thermocouples [Chopra et al. 1983].

Cermet films are primarily insulators with metal incorporated and are formed by: thermal and electron beam evaporation, co-evaporation, flash evaporation and co-sputtering techniques. It is widely believed that a multicomponent system like the cermet film consists of discrete metal islands dispersed in a continuous insulating matrix. Depending on the metal volume or atomic weight fraction, it is possible to characterize a cermet film by two different structural regions: metallic and dielectric.

When the metallic fraction is large, the metallic islands form a connected metallic network so that the carriers can percolate directly through the connected metal-islands. The micro-geometry of the metallic channels plays an important role in understanding the conduction mechanism in this regime. In the dielectric regime, at low metallic concentration, the metal grains form isolated islands in an insulating matrix. These films have similar structures to those of discontinuous metal films with a negative TCR. Depending on the size and spacing of the metallic grains as well as temperature of variation [Neugebauer 1962, Coutts 1969, Morris 1972, Hill et al. 1977, Schabowska et al. 1986, Sheng 1992] conduction in this regime may be due to thermally-

activated carrier hopping in which the charge carriers are transported from one metal island to another via tunneling. The transition between the metallic and dielectric regimes is characterized by a percolation threshold at which the metallic network first becomes disconnected. In general, such a transition occurs when the metallic volume fraction is below 40% [Morris 1972, Sheng 1992].

The identification of the dominant conduction mechanism is the key to understanding the electronic band structure of the material. Accurate knowledge of optical properties in conjunction with conductivity and Hall effect results are essential to understand the electronic transport properties in these materials. These topics are discussed in brief below.

1.1 Optical absorption

1.1.1 General features

The focus of optical absorption studies in both crystalline and non-crystalline materials is to obtain information on the density of states at the valence and conduction band edges, the optical band gap E_{opt} , the refractive index n , and the width E_g of the tail of the localized states. The theoretical works of Davis and Mott [1970] and Tauc et al. [1966] have generally established that for many amorphous materials, the absorption spectrum can be separated into two regions, shown schematically in fig. 1.1. These regions are created by transitions within the fully coordinated system perturbed to some extents by defects. A power law is followed at the highest energy (region 1) and a defect-induced exponential tail is present at the lowest energy (region 2).

The fundamental absorption takes place when an electron is excited by the absorption of a photon. There are two types of transition that can occur at the fundamental edge: direct and indirect. A direct transition is the vertical transition from valence band to conduction band in which a single photon is involved. An indirect transition involves the simultaneous interaction of a photon with lattice vibrations, in which one or more phonons are emitted or absorbed at the same time as the photon is absorbed. In this scenario, an electron transition takes place through a virtual state which is very short lived.

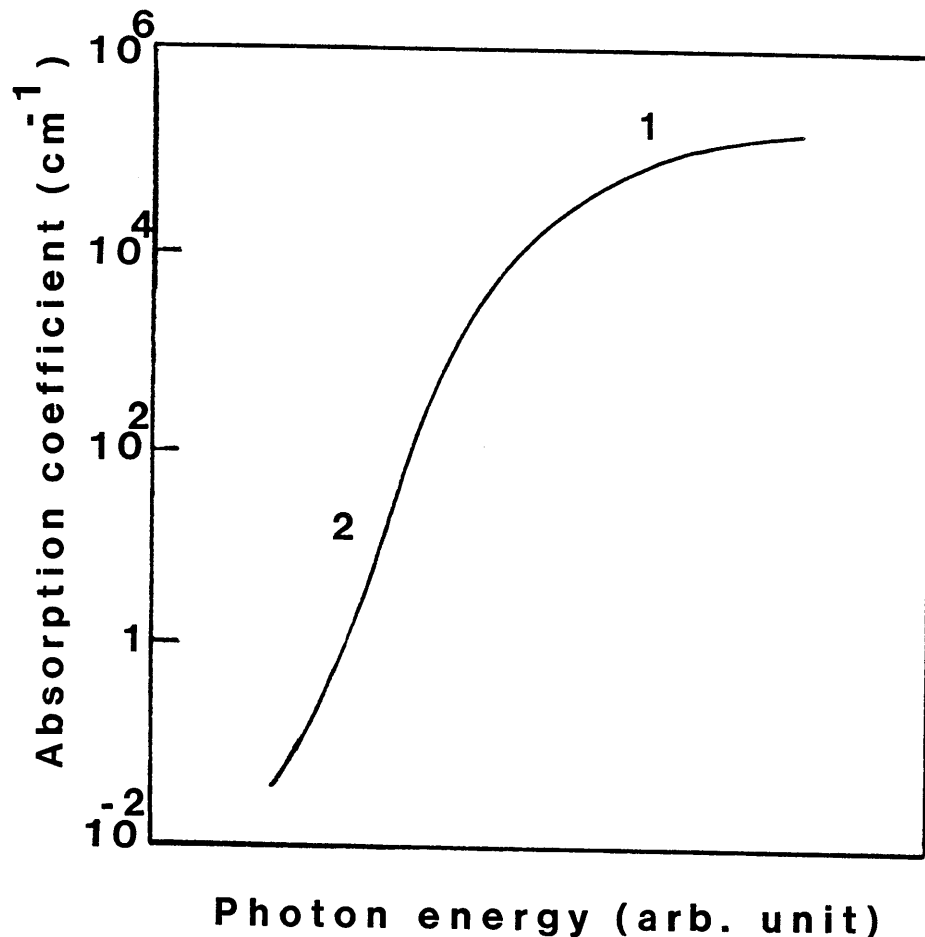


Fig. 1.1 : Schematic representation of the absorption edge of amorphous semiconductors.

1.1.2 Power law absorption region

In the high energy region 1, where the absorption coefficient $\alpha(\nu) > 10^4 \text{ cm}^{-1}$, it is assumed that the density of states beyond the mobility edges can be represented by a power law: $N(E) \approx E^{1/2}$ [Davis et al. 1970, Tauc et al. 1966]. In this case $\alpha(\nu)$, for direct transitions, can be written as,

$$\alpha(\nu) = \frac{B(h\nu - E_{opt})^n}{h\nu} \quad (1.1)$$

where ν is the photon frequency, h is Planck's constant and B is a constant. n has values of $1/2$, $3/2$, 2 and 3 , depending on whether the transition is allowed or forbidden. When the band edges are both parabolic and providing that energy is conserved during the absorption process, Tauc et al. [1966] propose that n should be equal to 2 . The origin of the power law and the meaning of E_{opt} has some controversy. In general, E_{opt} is interpreted as the optical gap i.e. the energy difference between valence and the conduction band mobility edges. However, it has been argued that the above expression (eqn. 1.1) is equally valid if transition takes place from the mobility edge at the top of the valence band to the tail of the conduction band [Davis and Mott 1970, Connell 1979]. In this case, E_{opt} will be smaller than that of the band to band transition. These opposing explanations can be resolved by the experimental determination of the E_{opt} , the width of the tail states and the thermal activation energy E_a . Nevertheless, this expression has been widely used to obtain E_{opt} in chalcogenide glasses [Mott and Davis 1979] and Oxide glasses [Moridi et al. 1977, Mansingh et al. 1978, Hogarth et al. 1981 and Al-Saie et al. 1993]. It has also been found that the equation (1.1) equally represents an accurate experimental observation with n equal to 2 when an in-direct transition takes place.

However, the quadratic energy dependence of $\alpha(\nu)$ is not universally observed. Amorphous Selenium [Davis et al. 1970] exhibits a linear energy dependence with $n=1$ and multicomponent chalcogenide alloys (Ge-As-Te-Si) show a cubic energy dependence [Elliot 1990]. According to Davis and Mott [1970], the linear dependence arises because of a very narrow range of localized states in a:Se. Furthermore, the density of states $N(E)$ may not be parabolic, as assumed by Tauc et al. [1966], but, instead, could be a linear function of E in the region of localized states in which case a cubic energy dependence may follow.

1.1.3 Exponential absorption region

The interband transition embodied in the expression for $\alpha(\nu)$ (eqn.1.1) implies the existence of sharp optical absorption edges. In reality, however, a gradual increase in $\alpha(\nu)$ has been observed (between 1 and 10^4 cm^{-1}) at the lower energy range. This region (marked 2 in fig 1.1) shows an almost linear relation on a logarithmic scale. Such behavior has often been referred to in the literature as the Urbach behaviour [Urbach 1953]. The so-called Urbach edge is found to have an exponential dependence on photon energy. With increasing sample temperature, the edge becomes broader, a behaviour which has been observed in many crystalline and non-crystalline materials i.e., silver halides, chalcogenide and oxide glasses [Mott and Davis 1979, Elliot 1990]. Despite this universal behaviour, the precise origin of this exponential absorption is uncertain.

Theoretical calculations tend to suggest that an exponential edge arises when the density of states in the tail states has the form $N(E) \approx \text{const.} e^{\beta E}$, where β is temperature-dependent given by $1/kT$ [Connell 1979]. This expression suggests a common origin for the Urbach edge

if β could have a fairly constant value for all amorphous materials. However, it has been suggested that β in amorphous semiconductors corresponds to the glass transition temperature T_g and, therefore, is unlikely to remain invariant from material to material. Redfield [1963] attributes this effect to frequency dependent fluctuations of microfields caused by impurities. This scenario is closely related to an electron impurity scattering process that results in lattice distortion and band-tail behaviour in amorphous materials. Tauc [1966, 1970] proposes that the disordered induced potential fluctuations arise from longitudinal optical phonons, frozen at the glass transition temperature. In that case, the frozen-in phonons will have the Gaussian distribution typical of T_g . The microfields so produced are sufficiently large to explain the values of β (about 10^{-25} eV^{-1}) in amorphous semiconductors. One implication of this hypothesis is that the defect-induced tail state widths will vary with the strength of the potential fluctuations; a consequence disputed by Davis and Mott [1970]. Their argument is based on some experimental observations that Urbach edges occur in many amorphous materials with roughly similar slopes (at room temperature) independent of the strength of impurity-potential fluctuations. Dow and Redfield [1972] suggest that the exponential behaviour arises from an electric field-induced broadening of an exciton line in the localized states. They calculated that fluctuations of microfields associated with impurities will create new states in the forbidden gap. The effect yields an absorption coefficient which has an exponential behaviour. This effect is closely related to the electron impurity scattering process resulting in an exponential behaviour.

It would appear from the foregoing discussion that no consensus exists as to the origin of the Urbach edge,

nor is there any definite agreement about the value of n in the power-law region. An interesting experimental and theoretical challenge is to determine which, if any of the above hypotheses correctly describes the physical situation in a particular material. The present experimental work is a modest effort in that direction.

1.2 DC Conduction Mechanism

1.2.1 Basic features

For many years the electronic transport properties of both crystalline and non-crystalline materials have been studied with remarkable theoretical and experimental advancements. A prominent feature of crystalline semiconductors is the presence of sharp band edges at the valence and conduction band leading to a well-defined forbidden energy gap. The result is a direct consequence of lattice periodicity and the presence of both short and long range atomic ordering in the crystal. The band structure is usually developed from the combined knowledge of electrical and optical properties. Amorphous semiconductors are characterized by the absence of long-range order. They do, however, maintain a high degree of short-range order. This has been confirmed by X-ray diffraction studies [Moss et al. 1970, Timken et al. 1973] which show that the nearest-neighbour arrangement in many amorphous materials is very similar to that in the crystalline state. As long as the short range order present in the crystalline phase is maintained in amorphous semiconductors, it is expected that some basic features of the electronic band structure will be preserved.

Small deviations in the bond lengths or bond angles quickly lead to the complete loss in translational symmetry after a few inter-atomic spacings. The absence

of long range order coupled with spatial fluctuations in the density of states create random atomic potentials (as opposed to the periodic potential in crystalline lattices). A direct consequence of this disorder is the formation of Anderson-localized states [Anderson 1958]. In a localized state, the only possible mode of transport is hopping. Hopping conduction is a term to denote the electrical conduction processes by a combined mechanism : thermal activation and tunneling. Wave functions are localized over a very short distance (≈ 1 nm) and the mobility drops to zero at $T=0$ even though the wave functions of the neighbouring states may overlap. Mott was the first one to show that these two seemingly independent processes can actually couple together to result in a non-activation type of behaviour [Mott 1968].

1.2.2 Band models

Several models have been proposed for the band structure of amorphous materials. The most prominent ones are the Cohen-Fritzsche-Ovshinsky (CFO) [Cohen et al. 1969] and Davis-Mott [1970] models. The CFO model proposes that the density of states consists of two overlapping band tails of localized states gradually decreasing from the band edges into the gap. The intersection of the two tails in the gap can lead to the creation of charged-defect states, and also leads to the pinning of the Fermi level in the middle of the gap. Localization near the band edges is due to short-range disorder resulting from small angle and bond-length fluctuations. Another feature of this model is the presence of a so called 'mobility edge'. This is the energy which separates localized tail states from the extended states in the band. In this model, the shape of the band edges is destroyed. Although the concept of a mobility gap is now widely accepted, the CFO model, with a continuous distribution of localized states throughout the gap, contradicts the sharp optical

absorption edge observed in many amorphous semiconductors [Stuke 1970, Mott et al. 1979, Elliot 1990].

The Davis-Mott model is quite similar to the CFO model except that the localized tail states are much narrower and extend for only a few tenths of an electron volt into the band gap. In addition to the tail states, there is a band of levels deep in the gap resulting from defects in the amorphous network. This is a more likely model for the density of states in amorphous semiconductors and is supported by a wide range of experimental work [Mott et al. 1979]. In 1972, Mott suggested that the observed mid-gap states might arise from broken or unbroken electron orbital, referred to as dangling bonds.

1.2.3 Small polaron model

In contrast to the CFO and Davis-Mott models, a different approach to the understanding of the electrical transport properties of amorphous semiconductors was suggested by Seager et al. [1972] and Emin [1973]. They contend that the charge carriers in some amorphous semiconductors may enter a self-trapped (small polaron) state as a result of the polarization of the surrounding atomic lattice. In general, a small polaron can move by two different mechanisms: at low temperatures, polarons can move without interactions with phonons, resulting in band conduction; at higher temperatures, the small polarons migrate by hopping between equivalent sites. Furthermore, an equivalent site is created by phonon-assisted lattice deformation and, therefore, the hopping motion can be regarded as a phonon-assisted tunneling process. The existence of mobility edges and tail states does not appear in the small polaron picture, where it is assumed that the electronic states form a small-polaron band. Many experimental works on a number of arsenic-based chalcogenide glasses [Seager et al. 1972, 1975; Emin et

al. 1972], on amorphous Si [Seager et al. 1974, Lewis 1976] ,on Au-SiO₂ cermet [Steele et al. 1992] and on Cu-GeO₂ cermet [Rahman et al. 1994] seem to lend considerable support to this model. Their observations raise serious doubts about the validity of the Davis-Mott or CFO models.

1.2.4 Island models

The electrical conduction mechanisms in granular metal films are usually explained in terms of Neugebauer-Webb [1962] and Hill-Coutts [1977] models. In the former model, conductivity follows an ohmic behaviour at low temperature and an exponential dependence on reciprocal temperature at higher temperature. An important concept of this model is that in the dielectric regime, an energy of the order of e^2/r , (where e is the electronic charge and r is the average linear dimension of the metal grain) will be required for carrier transfer from one initially neutral island to another some distance apart. Only carriers excited to states of at least this energy from the Fermi level will be able to tunnel from one neutral island to another. This process, therefore, will be an activated process with a well defined activation energy, depending only on the particle size. However, experimental works on a wide variety of metal and dielectric films suggest that the activation energy does show a rapid variation with temperature and that the conductivity shows a T^{-n} dependence with $n=0.3$ to 1, depending on the temperature of observation. This led Hill and Coutts [1977] to modify the Neugebauer-Webb model, in which the temperature dependence of particle size, inter-island distances and their influence on the conductivity, is considered. Many features of the observed conduction mechanism are found to agree with the predictions of this model [Morris 1972, Schabowska et al. 1986, Steele et al. 1987, 1988, Rahman et al. 1994].

1.2.5 Two channel model

Another possible model for interpreting DC conductivity is the two-channel model first suggested by Nagels et al. [1973]. When measured over a broad temperature range in chalcogenide glasses [Nagels et al. 1973, Seager et al. 1973, Mott et al. 1975], amorphous silicon [Le Comber et al. 1972], Au-SiO₂ cermet [Steele et al. 1987, 1988] and Cu-GeO₂ cermet [Rahman et al. 1994], the DC conductivity often shows strong curved lines at higher temperatures which gradually level out with decreasing temperature. This suggests that a single exponential of the form $\sigma \approx \sigma_0 \exp^{(-E_a/kT)}$ cannot represent the behaviour for the entire temperature range. The thermal activation energy E_a is no longer single-valued and is found to vary continuously with temperature. However, around a transition temperature T_c , both E_a and the pre exponential factor σ_0 show sudden jumps introducing a kind of kink in the conductivity curve. Le Comber et al. [1972] and Nagels et al. [1973] interpret this kink as an indication of two different conduction mechanisms operating simultaneously in the material. The two major features of their results are the weaker temperature dependence of the thermopower compared with the DC conductivity, a low thermally-activated Hall mobility, which increases with increasing temperature, and frequently exhibiting a sign opposite to that of thermopower. The two-channel model assumes almost equal contributions from two competing paths in which transport can occur almost simultaneously in extended and localized states. In particular, because the two paths contribute equally, one obtains a low (10^{-6} to 10 cm².V⁻¹.S⁻¹) and negatively-signed Hall mobility with P-type thermopower. The low mobility results from the cancellation of two relatively large mobilities of opposite sign. Both the small polaron model [Emin 1973], based on three-site geometry of the lattice atoms [Friedman and Holstein

1963], and the two-channel model provide a consistent physical basis for the essential features of the transport properties and are widely supported by an extensive network of experimental works [Le Comber et al. 1972, Nagels et al. 1973, Seager et al. 1973, Mott et al. 1975, Schabowska et al. 1986, Steele et al. 1987, 1988, Song et al. 1989, Rahman et al. 1994].

1.3 Hall effect

1.3.1 General remarks

The Hall effect plays an important role in the study of the electrical transport properties of semiconductors. In general, the DC conductivity is found to be strongly temperature-dependent at higher temperatures and is weakly activated at lower temperatures. However, one is unable to infer much about this behaviour from a conductivity measurement alone. To account for this behaviour, one must study those phenomena which yield more direct information about the carrier's transport mechanism. The study of Hall mobility is a valuable tool for this purpose [Emin 1973, Putley 1975]. In fact, Hall effect measurements in many amorphous materials do confirm that high temperature conductivity is primarily caused by the temperature dependence of the free carriers while at low temperatures, conductivity is governed by the carrier mobility [Le Comber et al. 1972, Emin 1973, Nagels et al. 1973, Seager et al. 1974, Mott et al. 1975, 1979, Vomvas et al. 1984, Elliot 1990, Steele et al. 1992 and Rahman et al. 1994].

In wide-band high-mobility semiconductors, where a single carrier dominates the transport mechanism, measurements of the Hall coefficient R_H is tantamount to a determination of the carrier concentration n . A combination of R_H with DC conductivity σ is responsible

for the mobility of the carriers. The sign of the Hall coefficient always equals the sign of the charge carrier.

In low mobility amorphous semiconductors, the interpretation of the Hall coefficient on this basis is not valid. This is because carriers have a mean free path comparable to the inter-atomic distance and, as a consequence, the ordinary transport theory based on the Boltzmann equation cannot be used any more [Nagels 1979]. In fact, the modern quantum theories of conduction mechanisms suggest that the interpretation of the Hall coefficient critically depends on the structure of the material, the nature of the electronic states involved in the motion of the carriers, and the specific conduction mechanism [Emin 1977]. For low mobility materials, the sign of the Hall coefficient associated with single-band conduction may be anomalous in the sense that it is not the same as that of the charge carrier. Differences in the sign of the carriers, as determined by Hall effect and thermopower measurements, have been reported for many amorphous materials [Seager et al. 1973, 1975, Emin 1974, Le Comber et al. 1977, Mott et al. 1979]. Three models are usually employed to account for this anomalous behaviour. These are the random phase model [Friedman 1971], the two-channel model [Nagels et al. 1973] and the small polaron model [Emin 1973].

1.3.2 Random phase and two channel models

The random phase model is based on the assumption that a three-site configuration is necessary for generating a Hall voltage. This model successfully predicts a sign anomaly as encountered in many amorphous semiconductors but, at the same time, predicts a temperature-independent Hall mobility which is at variance with many experimental observations [Le Comber et al. 1972, Seager et al. 1973, Nagels et al. 1973, Mott et al. 1975, Steele et al. 1992,

Rahman et al. 1994]. Nagels et al. [1973] used the two-channel model to interpret the p-n anomaly between the thermopower and the Hall effect measurements. Assuming nearly equal contributions from two conduction paths, this model predicts a temperature-dependent Hall mobility which increases with increasing temperature. At higher temperatures, carriers are excited to the mobility edge and, as a result, the Hall mobility should be temperature-independent, in agreement with the predictions of the random phase model. The low mobility and the sign anomaly in this model results from the cancellation of two relatively large mobilities of opposite sign. The idealistic assumption that both n- and p- type carriers may be present in a material in nearly equal proportion so as to render the Hall mobility very low appears to be unrealistic and, therefore, severely constrains the two-channel model.

1.3.3 Small polaron model

An alternative is the small polaron model initially developed by Friedman and Holstein [1963] for crystalline materials, and extended to non-crystalline materials by Emin [1973]. There may be some analogies to the Hall effect in the dielectric regime of cermet films. To generate a Hall field in the dielectric regime of a cermet, negatively and positively charged pairs of grains (islands) are necessary. Then, an electron on a negatively charged grain must have a choice of two or more neutral grains to which it may tunnel while in the magnetic field. The magnetic field breaks the symmetry and makes one site more favourable than the others. In this scenario, a minimum of three sites is required to generate a Hall effect. A three-site process can give rise to either negative or positive Hall coefficients, depending on the sign of the overlap integral of the electron wave functions centered on the grains [Friedman

et al. 1963; Emin 1973, 1977]. Friedman and Holstein [1963] utilized the occurrence probability approach in calculating the high temperature small polaron Hall mobility in the hexagonal lattice structure, which is composed of such three-site units. It was found that the sign of the Hall coefficient depends on the local geometry of the atoms. They found that the resulting Hall mobility is thermally-activated with an activation energy one-third of that associated with the conductivity or drift mobility. Furthermore, the Hall mobility will increase with increasing temperature reaching a maximum at $kT = W/3$ and will be smaller than the conductivity mobility. Here, W is the hopping activation energy.

In chalcogenide glasses like As_2Te_3 [Seager et al. 1973], and on a number of glasses containing significant fractions of As and Te [Seager et al. 1973, 1974, 1975; Nagels et al. 1973, Klaffe et al. 1976], the Hall mobility is observed to be thermally-activated with an activation energy one-third of that deduced from conductivity mobility and thermopower measurements. In these materials the Hall effect experiments suggest n-type carriers whereas thermopower experiments indicate p-type carriers. The experimental values of the prefactor σ_0 falls in the range $10^2 - 10^3 \Omega^{-1} \text{ cm}^{-1}$ and the hopping activation energy lies within the narrow limits 0.17 to 0.20 eV, while the Hall mobility possesses an activation energy of the order of 0.06 eV, being roughly one-third of the hopping energy. These results are consistent with the theoretical predictions of the small polaron hopping model.

Hall effect data of granular metal films are scarce. Extremely small Hall signals and high resistivity of the materials are among the factors which contribute to the experimental difficulties one encounters in these experiments. Early measurements on Au-SiO₂ and W-Al₂O₃

cermets [Sichel et al. 1982] and some recent measurements on Au-SiO_x [Steele et al. 1992] and Cu-GeO₂ cermets [Rahman et al. 1994] indicate that the small polaron hopping model is the dominant conduction mechanism in these materials. One recent exception is the Hall effects in vitreous V₂O₅-P₂O₅ glasses [Vomvas et al. 1984]. The DC conductivity in these glasses are known to occur via a thermally-activated small polaron hopping mechanism [Elliot 1990]. The Hall mobility increases with temperature in the temperature range of 320-500 K with no sign of a maximum, and the Hall mobility activation energy (0.2 eV) is found to be almost one-half of that of conductivity mobility (0.44 eV). These results are in clear contrast to the predictions of small polaron hopping theory. It would appear that Hall effects, and hence the DC conduction mechanism in amorphous materials, are not clearly understood.

1.4 AC Conduction Mechanism

1.4.1 Relaxation due to quantum mechanical tunneling

The temperature-dependence studies of DC conductivity and Hall mobility in amorphous materials provide information about the nature of the conduction mechanism. It is uncertain, however, to what extent these measurements reflect the bulk properties and to what extent they are affected by the irregularities and discontinuities of the amorphous atomic network; disorder in atomic configuration is thought to cause localized electronic states within the material. AC loss measurements are an important means by which information on these deep-defect states and the polarization response of the system can be obtained. Therefore, the AC measurements should be considered complimentary to DC measurements and not a substitute for them. Results of a large body of theoretical work [Pike 1972, Pollak and Pike 1972, Elliot

1977, 1987; Long 1982, Jonscher 1976, Mott and Davis 1979] and experimental investigations on chalcogenide glasses [Lakatos and Abkowitz 1971, Owen and Robertson 1970, Segawa 1974, Hauser 1983, 1985], on amorphous germanium [Narasimhan et al. 1976] and on SiO/SnO₂ films [Rahman et al. 1987] suggest that the AC conductivity generally varies as,

$$\sigma(\omega) = \omega^s T^n$$

where ω is the angular frequency of the applied field, T is the absolute temperature and s is a temperature dependent quantity whose value lies within $0 < s \leq 1$.

The origin of this apparent universal behaviour remains controversial. A variety of models based on quantum mechanical tunneling [Austin and Mott 1969, Long 1982] and hopping over the barrier [Pike 1972, Elliot 1977, 1987] have been suggested, none of which has been found to be entirely satisfactory. The conventional Quantum Mechanical Tunneling (QMT) model ascribes the phenomenon to relaxation caused by electrons or atomic tunneling between equilibrium sites. Two important features of this model are that AC conductivity varies linearly with temperature and the frequency exponent s is temperature-independent but frequency dependent. There are certain aspects of the Austin-Mott type QMT which do not conform to the experimental observations. Experimentally, s , in many amorphous materials has been found to lie between 0.7 and 1.0. s equal to 1.0 can only be obtained for unusually high values of the phonon frequency. The density of states near the Fermi level $N(E_F)$ calculated from this model lies in the range 10^{18} - 10^{20} $\text{eV}^{-1} \text{cm}^{-3}$. These values exceed those obtained from optical absorption experiments which are several orders of magnitude lower. Furthermore, $\sigma(\omega) \propto \omega^s$ behaviour (originally derived for chalcogenide glasses) has also

been observed in a number of insulating non-crystalline solids, such as SiO_2 [Rahman et al. 1987], Cu-GeO_2 [Rahman et al. 1994], a:Ge [Narasimhan et al 1976] and binary $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ glasses [Murawski 1984]. It was also observed that the AC conductivity becomes progressively less temperature-dependent with increasing frequency and that the measured AC conductivity approaches the DC value at high temperatures. These observations suggest the existence of other sources of dielectric loss mechanism, such as, inhomogeneities, defects, surface barriers and ionic dipoles which could give rise to the universal frequency-dependent behaviour [Elliot 1987].

An alternative model presented by Long [1982], based on small polaron tunneling, appears to explain some of the features observed in the lower frequency range $10^2\text{-}10^5$ Hz. In contrast to electron or atomic tunneling, this model considers the tunneling of carriers trapped at structural defects and predicts a frequency- and temperature-dependent tunneling distance which decreases more rapidly with increasing frequency than in the case of Austin-Mott type QMT. The tunneling distance and hence the AC conductivity are predicted to decrease sharply at sufficiently high frequencies [Elliot 1987, Long 1982]. Consequently, the frequency exponent, s , becomes temperature-dependent, increasing as temperature increases. The frequency dependence of the AC conductivity also suggests that s can become negative [Elliot 1987] below a cut-off frequency at which the tunneling distance reaches a minimum. This behaviour has been predicted to occur at a representative value of $10^6\text{-}10^8$ Hz. In reality, the tunneling distance cannot become less than the inter-atomic spacing, consequently at higher frequencies the small polaron tunneling contribution to the overall AC conductivity will become insignificant [Elliot 1987].

1.4.2 Relaxation due to hopping

The Correlated Barrier Hopping (CBH) model, originally developed by Pike [1972] to explain AC loss behaviour in scandium oxide thin films and later modified by Elliot [1977] to account for AC losses in chalcogenide glasses, sought to account for the discrepancies embodied in QMT. This model stipulates a bipolaron transport mechanism at lower temperatures and thermally-activated single polaron transport at higher temperatures ($T > 300$ K). This model predicts a relatively strong temperature-dependent AC conductivity resulting from the thermally-activated nature of the transport process. Furthermore, it predicts a slightly sublinear frequency-dependent $\sigma(\omega)$ yielding values of $N(E_F)$ much lower than those predicted by QMT, and a temperature-dependent S that decreases gradually from unity with increasing temperature. Such features have been observed in chalcogenide glasses [Mott and Davis 1979, Long 1982, Elliot 1977, Hauser 1983, 1985], transition metal oxides [Sayer et al. 1972, Murawski et al. 1974] and in crystalline vanadium dioxide [Mansing et al. 1984]. Some recent experimental works [Rahman et al. 1987, Gould et al. 1993] also indicate that the CBH model is very successful in accounting for the AC losses above $T > 300$ K. The CBH model does not appear to be valid below 300 K since it considers transport by classical hopping rather than quantum mechanical tunneling.

1.4.3 Resonant processes

Frequently in the higher frequency region i.e. $f > 10^5$ Hz, $\sigma(\omega) \propto \omega^s$ with s equal to 2 has been observed. The small polaron tunneling model appears incapable of explaining this result. Most works on amorphous materials point out that at high frequency there is another contribution to AC loss that does not involve QMT

relaxation [Mott and Davis 1979, Long 1982, Rahman et al. 1987, Islam et al. 1989, Elliot 1990]. In this resonant process, a phononless, but photon-activated electronic, transition can take place between two sites if the energy level separation of the sites is equal to the photon energy. A detailed calculation by Mott and Davis [1979] suggests that when the photon energy is significantly greater than the thermal energy kT , s varies with frequency and is independent of temperature. In this case the AC conductivity will have a quadratic frequency dependence deviating slightly from s equal to 2 because of a weakly varying logarithmic term in s .

One of the potential sources of difficulty in interpreting the AC loss data is the fact that the measured AC conductivity will have a contribution from DC conductivity at all temperatures. Since the AC conductivity of amorphous materials increases monotonically with frequency (at higher frequency) and is weakly dependent on temperatures, the AC loss will tend to dominate the DC conductivity at higher frequencies and lower temperatures. The DC conductivity is usually thermally activated, therefore, it will dominate the AC loss at high temperatures. Hence, in the high temperature region, the AC conductivity must be carefully decomposed from the dominating DC conductivity [Long 1982]. The mechanism of this decomposition depends on whether both AC and DC conductions arise from completely different processes or whether the same basic process is responsible for both types of conductivity. The results of DC conductivity in the present work (see Chapter 4) suggests that the small polaron hopping mechanism best describes the conduction mechanism. One purpose of studying AC conductivity, among other factors, is to investigate if the same basic mechanism is responsible for the AC conductivity.

1.5 Purpose of the work

It would appear from the discussions of the previous sections that much controversy exists surrounding the conduction mechanism in amorphous semiconductors. For cermet systems, this is further complicated due to the complex microgeometry of the metal islands dispersed in an insulating medium. This complexity is also the source of a rich variety of optical and electrical characteristics that has been utilized for a diverse array of applications [Ohring 1992, Sheng 1992].

While a tremendous amount of work has been done on a number of granular metal films in the past two decades, the exact nature of the conduction mechanism is still far from clearly understood. Accurate knowledge of the density of states at the valence and conduction band edges, the optical band gap, the width of the tail of localised states, the dc conductivity activation and hopping energies and the Hall effect results constitute important diagnostic tools for understanding the conduction mechanism. By combining optical, electrical conductivity and Hall effect data, a significant understanding of the conduction mechanism can be built up which will undoubtedly further unlock many new properties of the materials. To the knowledge of this author, no such comprehensive study has been performed on any of the cermet systems mentioned in the previous sections.

This thesis, therefore, constitutes an attempt to investigate the electronic transport mechanism in Cu-GeO₂ cermet system for the first time. It is the hope of this author that an elaborate analysis of the conduction mechanism in terms of optical, DC, Hall effect and AC results will lead to further understanding of many

transport properties now obscured by the complex microgeometry of the system.

FILM PREPARATION AND THICKNESS MEASUREMENTS

2.1 General considerations

A large number of deposition techniques for making thin films have been documented in the literature [Maisell 1970, Chopra et al. 1983, Pulker 1984]. The electrical and optical properties of thin films are extremely sensitive to deposition techniques and to a host of deposition parameters like thickness, deposition rate, and substrate temperature. Furthermore, the electrical and optical properties are very dependent on structural properties and the amount of impurities, vacancies, voids, dislocations, discontinuities and grain boundaries present; the type of defect which predominates depends on the deposition conditions and techniques used. The theories of nucleation and growth imply that the existence of discontinuous or continuous films depends on deposition rate, vacuum pressure, thickness, substrate temperature and crystalline nature of the substrate etc. [Lewis et al. 1978]. These very same parameters will also affect the microstructure of the films, resulting in an amorphous, polycrystalline or single-crystalline deposit.

Deposition methods are generally divided into two classes: chemical and physical processes [Maisell 1970, Pulker 1984]. In each process, formation of the films on a glass substrate can occur in a subtractive or additive way. Films obtained in a subtractive way are formed with the substrate in optical contact with the film; some of the films constituents are lost on the surface, leaving it porous and with an altered composition. Films formed in an additive way have the substrates coated during

deposition. In such techniques, the adhesion of the evaporant particles to the glass surface is good, making the process very neat and compact. Since, in the present work, deposition is achieved by the electron beam evaporation process, the chemical subtractive and additive processes will not be discussed further.

2.2 Deposition techniques

Thin films of materials such as alloys, compounds and mixtures of different constituents can be produced in crystalline or amorphous state by evaporation on an appropriate substrate. The mechanism involved in forming the film may be purely physical, i.e. simple evaporation, or may involve chemical reactions. The technique of forming thin films by condensation at very low pressure has been developed in parallel with the industrial development of techniques of producing high vacuum in large volumes using pumps of very high speed. Films obtained by evaporation are usually made at high pressures $\approx 10^{-3}$ to 10^{-5} Pa and in some cases to ultra high vacuum at 10^{-7} Pa. This is combined with fast deposition rates which reduce contamination and concentration of impurity atoms in the films.

There are a number of techniques for facilitating physical vapour deposition. These include resistive evaporation; electron beam evaporation; co-evaporation; flash evaporation; sputtering and ion planting. Physical vapour deposition involves three steps [Pulker 1984] :

1. Vapour generation by thermal or electron beam evaporation, sublimation or sputtering;
2. Elimination of the effects of impurities, voids and discontinuities on film composition and properties require clean vacuum condition and appropriate

residual atmospheres. When the vaporized particles travel from the source to the substrate through a reduced atmosphere, collision with residual gas molecules becomes minimal, thus improving the purity and homogeneity of the material.

3. Condensation occurs on the substrate through the processes of nucleation and growth, possibly during high energy particle bombardment.

There are a variety of methods that can be employed for film evaporation. The choice of method usually depends on the materials used, the evaporation temperature and the required film purity.

2.2.1 Indirect resistive evaporation

This is an often used technique where the evaporation material, placed in a boat or crucible, coil or strip, is heated by a current. This method is quite suitable for a number of alloys and compounds. However, if these materials are in powder form, sputtering and scattering of the particles occur due to the sudden release of gas on heating. This will create an imbalance in the rate of evaporation of the material. Furthermore, if the initial material consists of two different materials (like Cu and GeO_2 in powder form) with different melting points of the constituents, the evaporation rate for each material may be different. Consequently, the composition of the deposited film may differ greatly from that of the starting compound or alloy. Film contamination resulting from a chemical reaction between the boat material, reactive gases and the evaporant material itself may also occur.

2.2.2 Co-evaporation technique

The problems encountered in resistive heating are partially solved in the co-evaporation technique. This method is suitable for evaporating a mixture involving constituents with different melting temperatures. The technique involves co-evaporating the constituents separately from two different boats maintained at appropriate temperatures while the substrate itself is maintained at a temperature appropriate for condensation. This method, although it produces highly pure or exact stoichiometric compound deposits, has a number of problems associated with it. First, it is costly, as it requires separate power supplies and a provision to maintain the boat temperature constant and the vapour densities of the constituents near the substrate. A major concern is to maintain the position of the substrate relative to the angle of emission of the two sources; compositional inhomogeneity may result if the substrate is not at the same inclination relative to both the sources. Even if this is achieved, a lateral variation of the composition will occur, with each end being relatively rich in the component whose source is situated near to it. In addition to the above, the risk of obtaining large deviations from stoichiometry is potentially greater if both constituents have substantial solubility in compound form.

2.2.3 Electron beam evaporation from a single source

The problems encountered in co-evaporation can be partially removed in this technique where the materials (elements, compounds and alloys etc.) can be evaporated from a single boat, thus eliminating the need for a cumbersome network of power supplies and thickness monitoring devices. This method has been established as a universal method for producing highly pure films. **This**

technique is chosen in the present work for the reasons that it is clean, easy to operate and has a minimum number of parameters to be controlled. First, the starting materials Cu and GeO₂ in fine granular form are crushed repeatedly in a porcelain crucible to achieve the desirable uniformity in the composition. The mixture is then pressed into disc shape samples in a vacuum of about 1.3 Pa under a pressure of 8 tons weight. The material is then placed in a graphite boat inside an Edward 306 A coating system where it is heated by an electron beam. The high energy electrons, emitted from a hot filament (cathode) and accelerated by a strong potential difference (4000 V) towards the graphite boat (anode), produce a very high temperature (about 1500 to 2000°C) on the surface of the evaporating material, so that metal grains (Cu) and dielectric grains (GeO₂) can be evaporated simultaneously. The advantage of this technique is that a small amounts of evaporated material from the hot filament are unable to contaminate the film. The disadvantage is a low evaporation rate and a slight non-uniformity in the thickness. However, to avoid the latter problem, the substrates were positioned centrally so that the rate of arrival of the evaporant materials was uniform. Furthermore, to ensure uniformity in film composition, the Cu-GeO₂ mixtures were slowly melted initially with a mechanical shutter covering the source. Time was allowed for uniform alloy to be formed before increasing the current to produce evaporation.

The deposition was made at a vacuum of 10^{-3} to 10^{-4} Pa and at a substrate temperature of 303 K. The substrate temperature was monitored with the help of a built-in temperature controller in the evaporation system. An appropriate height of the substrate relative to the source was determined by evaporating films on a trial and error basis against accelerating voltage and pressure. The best height was determined when clean and clear films

were produced at a deposition rate of 3 nm/s, corresponding to a beam current of 15 mA in an approximately equal interval of time.

2.2.4 The flash evaporation technique

It is difficult to achieve a homogeneous film, in structure or in thickness, using electron beam evaporation with cermet, alloys or mixtures, where evaporant materials consists of constituents with different melting points. As mentioned earlier, the co-evaporation technique can overcome some of these difficulties but the process involves a complicated and expensive set-up. In the flash-evaporation technique, problems encountered are solved in a cheaper and efficient way. In this technique the starting material is taken in powder form and dropped steadily onto a resistively-heated boat maintained at a temperature suitable for instantaneous evaporation. In this method the different vapour pressures of the constituent materials play a negligible role only and a homogeneous film is generally obtained after condensation [Maissel et al. 1970, Baynes 1983, Pulker 1984].

However, there are some important disadvantages of this technique. Inhomogeneity in film composition will result if a steady trickle of the mixture is not maintained. Furthermore, the boat temperature must be considerably higher than the evaporation temperature of all constituents so that instant evaporation takes place. With a cermet-like material, where a high evaporation temperature is required, a resistively-heated boat source may be inappropriate and instead an electron gun source may be a better choice. Another disadvantage is that under instantaneous evaporation, fractionation of the evaporant particle might occur, resulting in stratification in the film. Other problems are powder

ejection or sputtering by the sudden release of gas resulting from rising vapours of the evaporant. Powders may also bounce off the boat on impact, resulting in a non-uniform evaporation rate. Sputtering generally increases with an increasing evaporation rate, setting a limit to the maximum evaporation rate attainable.

2.2.5 The sputtering technique

Sputtering techniques, both DC and RF, are widely used for metals, alloys and cermets and are often preferred in large scale production. In this method, two electrodes are installed in the vacuum chamber (pressure $\leq 10^{-3}$ Pa); the cathode is made from the desired material. The substrate holder, which can be earthed or maintained at a floating potential, is the second electrode. Argon, nitrogen, oxygen or a mixture of these gases are normally used as sputter gases. Positive ions produced in a gas discharge ignited at a pressure between 10^{-1} and 1 Pa, hit the cathode and through a momentum transfer process eject mainly neutral particles from the cathode [Pulker 1984]. These particles then deposit on the substrate. The basic requirements for the successful implementation of this method requires an identical sputter rate of constituents. Essentially the method is slow and the possibility of gas ions or atoms being trapped in the film can not be eliminated [Glang 1970].

2.3 The evaporation system

An Edwards vacuum coating unit model E 306 A (plate 1) was used for the deposition of the thin films. The system consists of a glass bell jar evacuated by a water-cooled diffusion pump with liquid nitrogen trap to the maximum vacuum of 10^{-5} Pa and is backed by a rotary pump. The chamber gadgetry consists of a 4-position multifilament turret which produces sequential evaporation of the

materials by resistive heating using a 10 V, 90 A low tension power supply. The source includes molybdenum boats, tungsten helical filaments, tungsten baskets and tungsten hair-pin filaments etc. This technique was employed to evaporate aluminum electrodes on to the films using tungsten helical filament as a source. Since, Cu-GeO₂ cermets were found to have high melting points (about 1000°C), the resistive heating technique was not adequate to produce the films. Therefore, the 4-position multifilament turret was replaced by an electron beam gun in order to produce uncontaminated rapid evaporation. The accessory comprises a six-hearth turret with rotary drive for sequential evaporation and an electron beam gun mounted on a baffle plate. The system utilizes a 3.3 kV, 50 mA HT power supply complete with HT voltage and emission current meters with variable transformers for control. Graphite boats were used as source.

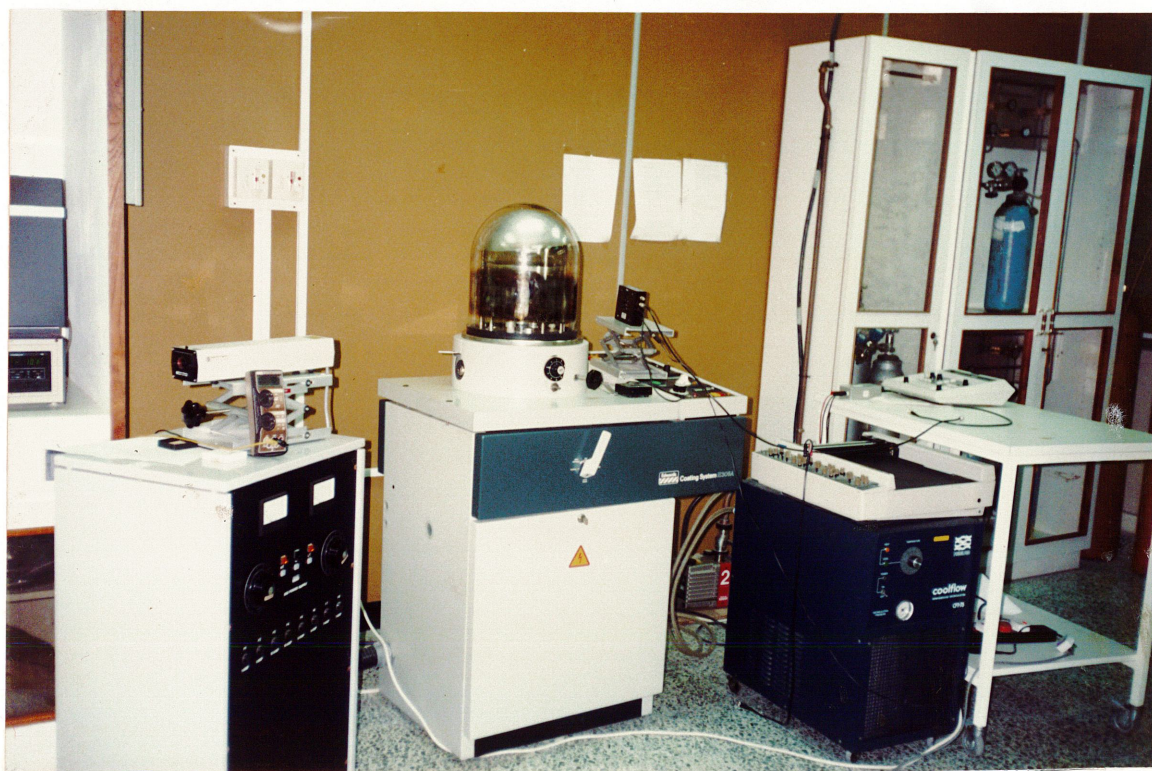


Plate 1 : Edwards E 306 A evaporation system

Prior to deposition, Corning 7059 glass substrates, centrally positioned about 13 cm above the source, were heated to prevent adsorption of contaminants and to remove moisture trapped in various gadgetry. The heating gadgetry comprised a sheathed heater coil, reflector and spherical work-holder, a thermocouple, a meter to indicate the substrate temperature and a regulator. The regulator permits temperature adjustments to values in excess of 300°C. The substrate, and chamber itself was heated under vacuum (10^{-2} Pa) for about 10 minutes and was left to return to room temperature. In this way a moisture-free environment was ensured.

All the evaporations were carried out at a substrate temperature of 303 K. A mechanical shutter, in addition to being used for accurate commencement and termination of the evaporation, also served as a shield to prevent heat radiation and volatile constituents from reaching the substrate during the source-degassing and melting (of the material) period. The evaporation rate and thickness were monitored first using the transmittance and reflectance method with a He-Ne laser beam and then by a water-cooled oscillating quartz crystal mounted near the substrate area. The thickness monitoring techniques are described in some details in sections (2.5.1), (2.5.2) and (2.5.3).

2.4 Evaporation of Cu-GeO₂ thin films

2.4.1 Substrate cleaning

Prior to deposition, Corning 7059 glass slides were cut into appropriate dimensions. They were then cleaned ultrasonically in a ultramet detergent bath for 30 minutes at 30°C. The slides were next rinsed in distilled water. After this step, the slides were ultrasonically cleaned in a trichomethylene bath for 30 minutes at 30°C.

They were then rinsed in distilled water and cleaned ultrasonically again in a distilled water bath. The slides were then dried with a compressed air gun. To ensure the removal of any residual moisture, the substrates were exposed to a glow discharge in the vacuum system (10^{-1} Pa) prior to the deposition.

2.4.2 Deposition of the films

Prior to deposition, the starting materials Cu and GeO_2 powders (in atomic weight concentrations), were ground repeatedly in a porcelain crucible for about 10 minutes. The mixture was then pressed in vacuum at 8 tons pressure in the shape of discs. This was necessary to avoid sputtering of the material under the impact of an accelerated electron beam. The disc was then transferred to the vacuum chamber of the coating system and placed in a graphite crucible. When a good vacuum ($\leq 10^{-3}$ Pa) and the appropriate substrate temperature (303 K) were achieved, the resulting pellets were heated to a temperature slightly less than the normal evaporation temperature. During this procedure, the mechanical shutter was in place over the crucible. The pellet and the filament were thereby degassed for about 5 minutes to achieve desired equilibrium condition in the chamber. During degassing, the chamber pressure was found to decrease slightly from 10^{-3} to 5×10^{-3} Pa. A waiting period was allowed on and off for the desired pressure to be achieved. When the degassing period was completed, the HT voltage was increased slowly to 4kV. Then the emission current was slowly increased to 12-15 mA with the mechanical shutter still closed. The HT and LT power supplies were continually adjusted to obtain the best operating conditions (e.g. minimum fluctuations in the vacuum pressure, no sudden sputtering of the material etc.). Once that was achieved, the shutter was removed and the deposition process was started in conjunction

with in-situ thickness and deposition-rate monitoring using a Edwards FTM5 quartz crystal thickness monitor. During the deposition process, the chamber pressure, temperature and the deposition rate were continually checked in order to ensure uniformity of the films. With a typical rate of 3 nm/s, a 410 nm thick coating was produced in about 140 s. After the deposition was completed, the mechanical shutter was closed and the emission current was lowered to zero.

Coatings were also made on silicon-wafers for infrared studies (see Chapter 3). Following identical deposition conditions and procedures, about 100 films were produced at different stages for the optical and electrical investigations. Initially, samples of different thicknesses A(227 nm), B(340 nm) and C(407 nm) were obtained for the composition 30 at.wt.% Cu-70 at.wt.% GeO₂ for the optical and two-probe DC conductivity studies. In the second stage, films of different compositions (5 to 30 at.wt.% Cu) having the identical thickness of 410 nm were produced for 4-probe DC conductivity, Hall effect and AC conductivity studies.

In order to improve the accuracy of thickness measurements, two other methods based on optical transmission and reflection interference fringes were utilized. Because thickness is an important parameter which effects the accuracy of all other experimental results and, consequently, the electrical and optical properties, details of the measurements and calculations are outlined in section (2.5).

2.5 Thickness measurements

Thickness is an important parameter which appears in many equations that characterize thin films. Errors or uncertainties in thickness will adversely affect a host

of optical, electrical and thermal properties of the material. It is for this reason that an accurate determination of thickness is essential. With highly sophisticated film thickness measuring techniques developed over the years [Maisell 1970, Swanepoel 1983, Pulker 1984], it is now possible to carry out measurements during, and after, the deposition. A number of mechanical and optical techniques are available for thickness measurements. However, apart from a few exceptions, semiconductor dielectric material thicknesses are mostly measured by optical methods. One advantage of this method is that the layers are probed by optical beams which leave the surface and the structure intact. In-situ measurements utilized to determine the precise knowledge of thickness at any point of time during the deposition can be carried-out by utilizing either of the two methods. Furthermore, simultaneous measurements of the rate of deposition and thickness are essential, for both these parameters greatly effect the electrical and optical properties. From this point of view, commercially available thickness and rate monitors integrated in an automatic process control are of great importance. In the following, three methods which were utilized for thickness determination are outlined.

2.5.1 Optical reflectance and transmittance method

During the deposition, the film thickness can be monitored optically by transmitted and/or reflected light interference using a photo-sensor. Provided that the refractive indices of the films and the substrate are different, interference of waves reflected from different layers of the films (as the thickness increases) can give rise to pronounced maxima and minima. The periodic change in the reflection and transmission of an optical beam with increasing thickness gives rise to the following

relation between geometric thickness t and the optical thickness nt of a film [Pulker 1984] :

$$t = X \frac{\lambda}{4n} \quad (2.1)$$

where λ is the wavelength of the incident light, X is the number of reflection and transmission peaks, and n is the refractive index of the material.

A typical measuring arrangement is shown in fig. 2.1. A He-Ne laser beam is reflected from the layers of the film and is detected by a photo-sensor, the output of which is then fed to an X-Y recorder via a lock-in-amplifier. An example of this kind of plots is shown in fig.2.2. The use of a highly coherent and monochromatic laser beam together with a light chopper eliminates interference from day-light and light emitted by the evaporation sources. A few instruments like the Balzer GSM 210 and Honeywell thickness monitors have been built employing this technique [Pulker 1984]. The thickness and the deposition rates are calculated from the curve in fig. 2.2. As thickness increases, the number of reflection and transmission peaks increase as a function of deposition time. Therefore, thickness at any instant has to be determined as the tracing of the curve is in progress and accordingly, the process has to be terminated when the desired thickness is reached. Furthermore, the LT current regulator has to be manually controlled in a manner to ensure an uniform X-Y sweep and the deposition rate. These steps need to be carried out carefully and often need several trials before a desired result can be obtained. Fig.2.2 show the curves obtained for 227 and 340 nm thick films.

A major disadvantage of this technique is that the refractive index n of the material corresponding to the laser wavelength (632.8 nm) has to be determined

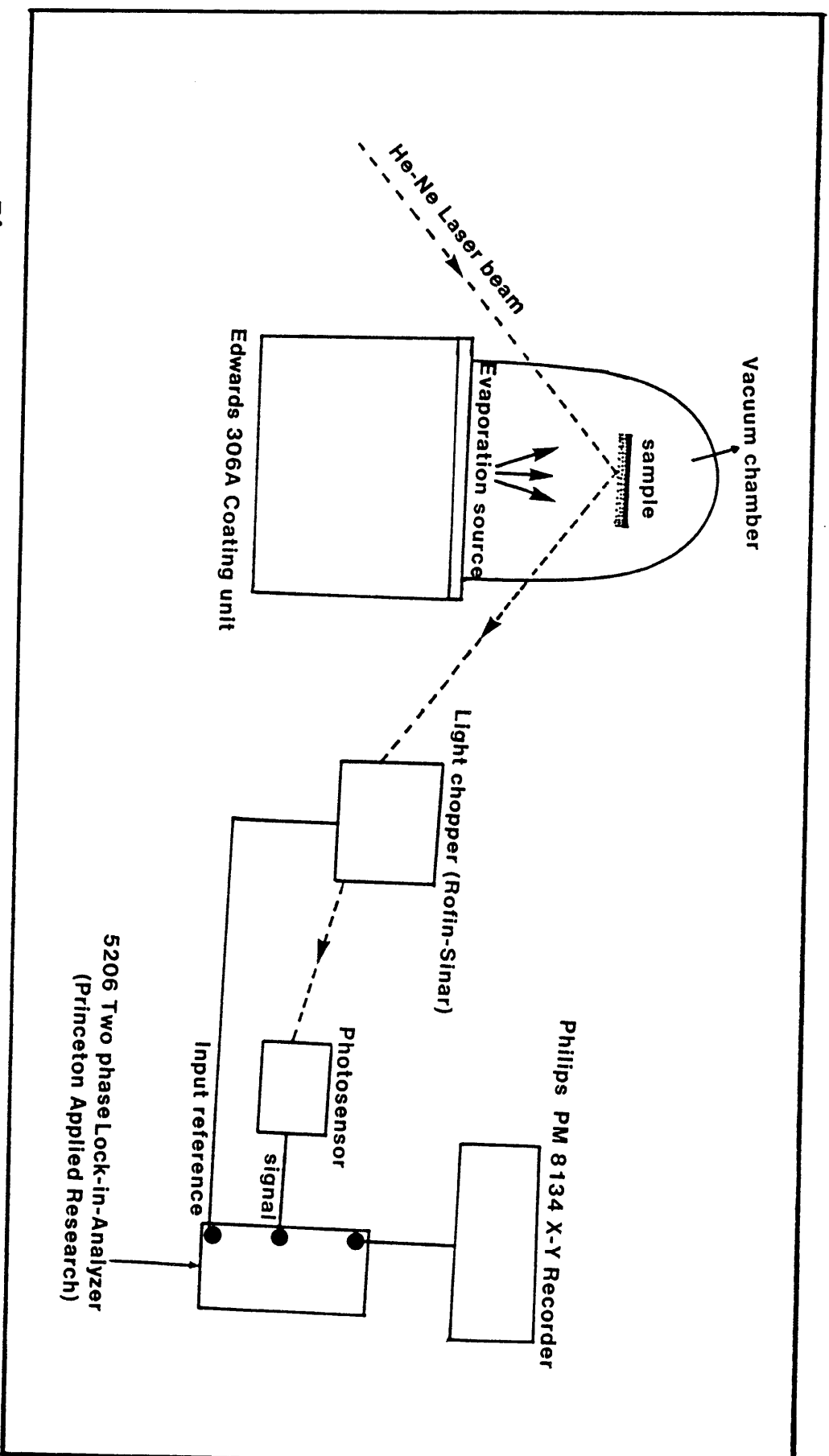


Fig. 2.1 : Measuring arrangement of the film thickness by optical reflectance and transmittance method.

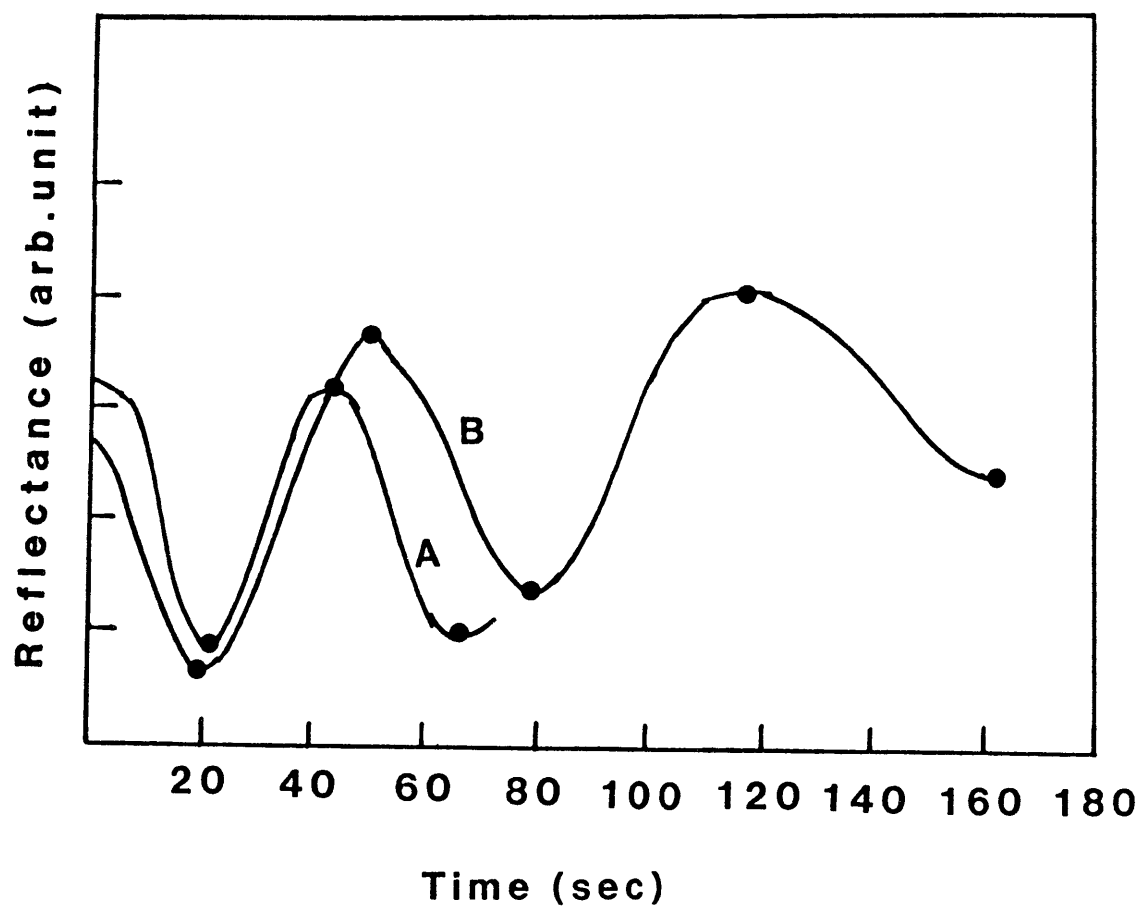


Fig. 2.2 : Reflectance as a function of growth time of the films A and B. Number of reflection and transmission peaks, X , and thickness, t , are according to eqn.(2.1).

(A) $X=3\frac{1}{3}$ (B) $X=5$

separately from the transmission interference fringes employing Swanepoel [1983] technique (see section (2.5.3)). Using that technique, n at the laser wavelength was found to be 2.32. From fig. 2.2 one notes that $X = 3\frac{1}{3}$ and $X = 5$ for samples A and B, respectively, which when substituted into equation (2.1), together with the value of n , yields thicknesses of 227 nm and 340 nm. The mean rates of deposition were calculated to be 3.24 nm/s and 3.00 nm/s respectively.

Achieving identical thickness and deposition rates with this technique is extremely difficult. Hence, this method was abandoned and all subsequent thickness measurements for the optical and electrical studies were performed with a microprocessor controlled quartz-crystal monitor. The thicknesses were later confirmed from the interference fringes of the transmission spectrum. These two techniques are described in brief in the next two sections.

2.5.2 Thickness measurements by quartz crystal monitor

The problems encountered in the previous section in monitoring the thickness and the deposition rate accurately were overcome by using an Edwards's FTM5 thickness monitor in conjunction with a water-cooled oscillating quartz crystal unit fig.(2.3). The quartz crystal microbalance technique has been in use ever since the idea was first proposed by Sauerbrey [1955] and Lostis [1959]. They had assumed that the elastic properties of the quartz crystal are not affected by the deposited material and that as the deposited layer increases, the frequency of the crystal's oscillations decreases. This principle, in some modified form, has been used by Edwards [1986] and other industrial manufacturers like Balzers and Honeywell. In developing the microbalance technique Sauerbrey [1955] assumed that

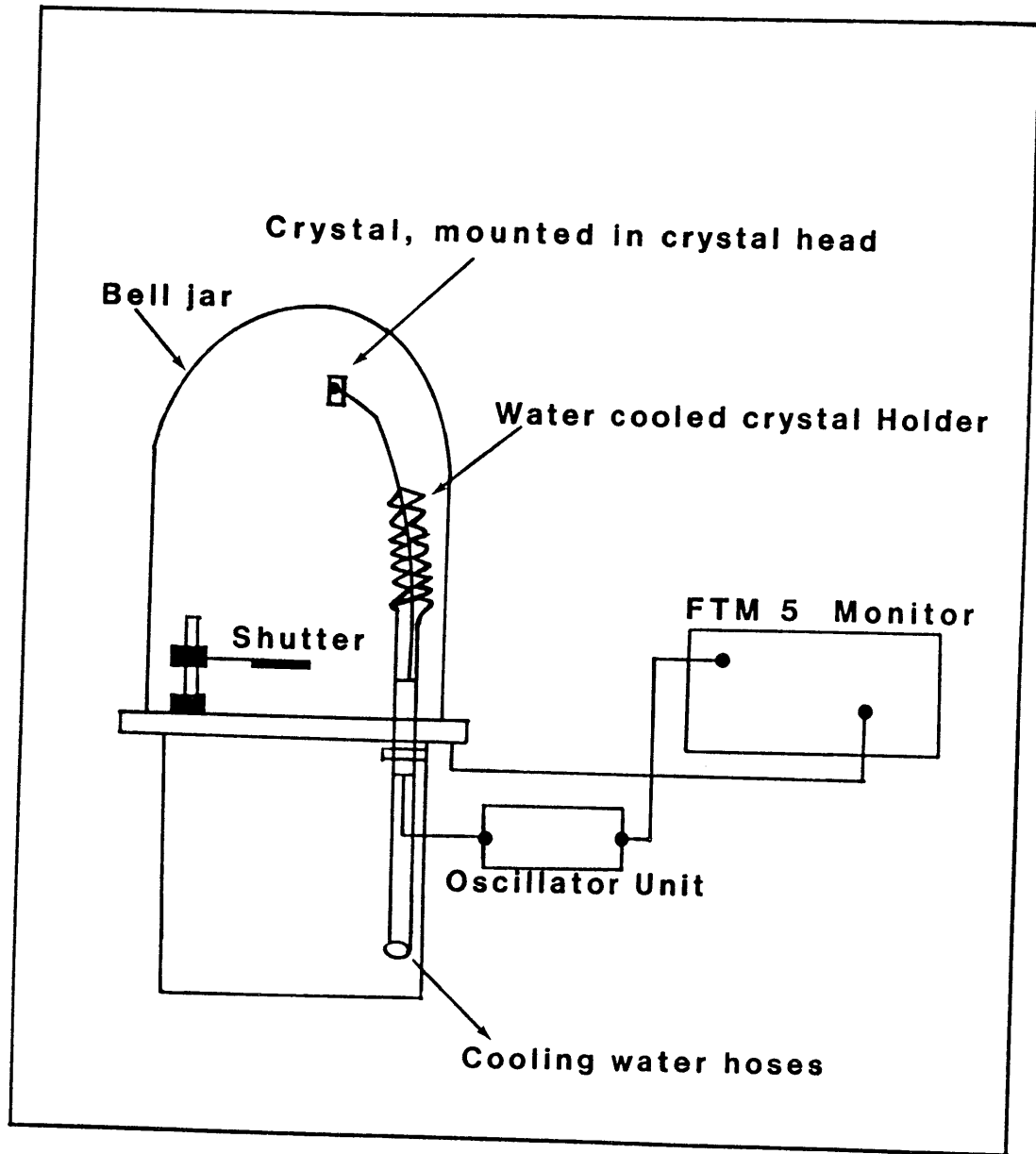


Fig. 2.3 : Measuring arrangement of the Edwards quartz crystal FTM 5 thickness monitor.

as the film thickness increases, the addition of film mass can be treated as an equivalent mass-change of the quartz crystal itself and that the elastic properties of the deposited material are the same as those of the quartz crystal. His relation for the frequency change of the loaded crystal is [Pulker 1984]

$$\frac{\Delta \nu}{\nu} = -\frac{m_f}{m_q} \quad (2.2)$$

Here ν is the frequency of the loaded crystal, m_f is the area-mass density of the deposited material, and m_q is the area-mass density of the quartz crystal. These assumptions are found to be valid as long as the crystal detectors are not heavily loaded. In fact, Pulker [1984] estimated that the Sauerbrey hypothesis is valid if $m_f/m_q \leq 2\%$.

With second generation instruments, resulting from advancements in digital electronics and sensor crystals, thicker depositions lead to $m_f/m_q \leq 25\%$, and Sauerbrey's original assumptions are not valid. A more rigorous acoustic analysis of the compound resonator formed by the quartz crystal and the deposited film leads to the following equation [Miller and Bolef 1968, Lu et al. 1972],

$$\tan \frac{\pi \nu}{\nu_q} = -\frac{\rho_f \nu_f}{\rho_q \nu_q} \tan \frac{\pi \nu}{\nu_f} \quad (2.3)$$

where ν is the continuous acoustic wave frequency propagating from the quartz into the deposited film, ν_q the frequency of the oscillating quartz, ν_f is the mechanical resonance frequency of the deposited film, $V_f (= 2t\nu)$ is the shear wave velocity in the film, t is the film thickness, ρ_f is the density of the film, ρ_q is the density of the oscillating quartz, V_q the shear wave

velocity in the quartz crystal, $\rho_f V_f$ is the acoustic impedance Z_f of the film and $\rho_q V_q$ the acoustic impedance Z_q of the quartz. Equation (2.3) suggests that the compound resonator frequency ν is dependent on the ratio Z_f/Z_q implying that materials with different elastic properties must obey different mass-frequency relations. This correction factor must be included in Sauerbrey's formalism.

However, for highly loaded crystal i.e. for $Z_f=Z_q$, the usual Sauerbrey equation (2.2) is an approximation to the Miller-Bolef equation (2.3). Edwards use microprocessor technology to incorporate Miller-Bolef equation into the FTM5 thickness monitor unit [Edwards 1986]. It is obvious from equation (2.3) that for accurate monitoring of thickness and deposition rate, the density and acoustic impedance of the film material are two vital parameters.

In the present work the density of the bulk Cu-GeO₂ cermet (formed by melting the mixes in the vacuum chamber) was found to be 4.5 gm/cm³ but no accurate value of the acoustic impedance could be obtained. As a result, a default value $Z_f = 8.834 \times 10^5 \text{ g.cm}^{-2}.\text{s}^{-1}$ was used instead [Edwards 1986]. The FTM5 has the following specifications:

Thickness range	: 0 to 999.99 μm , resolution 0.1 nm
Rate of deposition range	: 0 to 999.99 nm/s; resolution 0.1 nm/s
Acoustic impedance	: 1.0 to 99.9 $\times 10^5 \text{ gm.cm}^{-2}.\text{s}^{-1}$
Crystal dimension	: plano-convex plate, 14 mm diameter, 0.3 mm thick.

Unloaded crystal frequency: 6 MHz

Materials accessories : Quartz, gold plated electrodes, Oscillator unit, Water cooled crystal holder.

The water-cooled crystal holder is used in conjunction with a crystal, an oscillator unit and the FTM5 microprocessor (fig.2.3). The crystal is held in a water-cooled environment to shield it from radiated heat and to remove heat gained from the deposited layer. The oscillator unit contains an oscillator circuit, the oscillating frequency of which is controlled by the natural frequency of the crystal. As the film thickness increases on the crystal, the natural frequency decreases together with the output frequency ν of the oscillator. The change in the frequency is detected by the thickness monitor which converts the frequency change into deposition rate and thickness information.

2.5.2.1 Determining the tooling factor

Geometries related to the position of the substrate and the crystal-head with respect to the evaporation source will lead to an incorrect estimate of the thickness. A tooling factor can be set to compensate for this difference which can be calculated by experimental calibration. Edwards [1986] defines the tooling factor as follows:

$$\text{Tooling} = \frac{T_{\text{real}}}{T_m} \quad (2.4)$$

Here T_{real} is the actual thickness deposited on the substrate and T_m is the thickness recorded by the monitor. A tooling factor of 1.0 implies that the sensor and substrate receive the same deposit thickness: a larger tooling factor implies that the sensor receives a thinner

deposit than the substrate. The actual calibration was carried out as follows:

First, the known density ρ , the acoustic impedance Z and a tooling factor of 1.0 were entered into the memory of the thickness monitor. A new crystal is placed in the water cooled head and two substrates, appropriately masked, were held centrally relative to the evaporation source. The crystal-head was placed as near and as level as possible to the substrate. A thin deposition of about 80 nm (T_m) was made on the substrate. The actual thickness (T_{real}) deposited on the substrate was later found using transmission spectroscopy (section (2.5.3)).

In the present investigation a tooling factor of 3.5 was calculated and entered into the memory of the monitor. Care was taken not to overload the crystal since the acoustic impedance factor becomes very important in this case. To this end, a deposition was carried out on a fresh crystal until it ceased to oscillate. The thickness and the time of deposition was noted. In the actual investigation, all depositions were carried out (at the same rate) for a much shorter time to ensure that the crystal was not loaded.

After recording the thickness in-situ by FTM5 thickness monitor, it was again confirmed by transmission spectroscopy in an effort to improve the accuracy and to determine the refractive index of the material at a given wavelength. It was found that the later method yielded thickness values which were about 2 to 20% lower than that obtained using the quartz crystal monitor. Therefore, a mean value of the thickness was calculated using two measurements for all the samples.

2.5.3 Swanepoel method of interference fringes

As mentioned in the previous section, a quartz crystal monitor needs to be calibrated in terms of known density, acoustic impedance and a tooling factor. The tooling factor eliminates the geometrical effects arising from the positions of the substrates and the crystal head relative to the evaporation source. However, to determine the tooling factor, thicknesses of the trial films needs to be known accurately. Therefore, Swanepoel's [1983] technique, which is based on creating an envelope to the transmission maxima and minima, was utilized for two purposes. First, it was used to calibrate the FTM5 thickness monitor, secondly the technique was used independently to confirm the thickness monitored by the quartz crystal micro-balance and to obtain the refractive index of the material. The advantage of this technique over other optical methods is that it does not assume the values of the refractive index to determine the thickness. Rather, $n(\lambda)$ can be determined from the same transmission spectrum.

Swanepoel [1983] manipulated the basic equations for reflectance, transmittance and transmission interference fringes of a thin film (formed on a transparent substrate) to derive expressions for $n(\lambda)$ and the absorption coefficient $\alpha(\lambda)$. The following is a brief review of the procedure:

Consider a thin uniform film on a transparent substrate fig. (2.4a). The air, the film and the glass substrate are all considered to be homogeneous and optically isotropic with refractive indices n_0 , n , and S , respectively. The complex refractive index of the film is given by,

$$\hat{n}(\lambda) = n(\lambda) - iK(\lambda) \quad (2.5)$$

where K is the extinction coefficient given by,

$$K = \frac{\alpha(\lambda)\lambda}{4\pi} \quad (2.6)$$

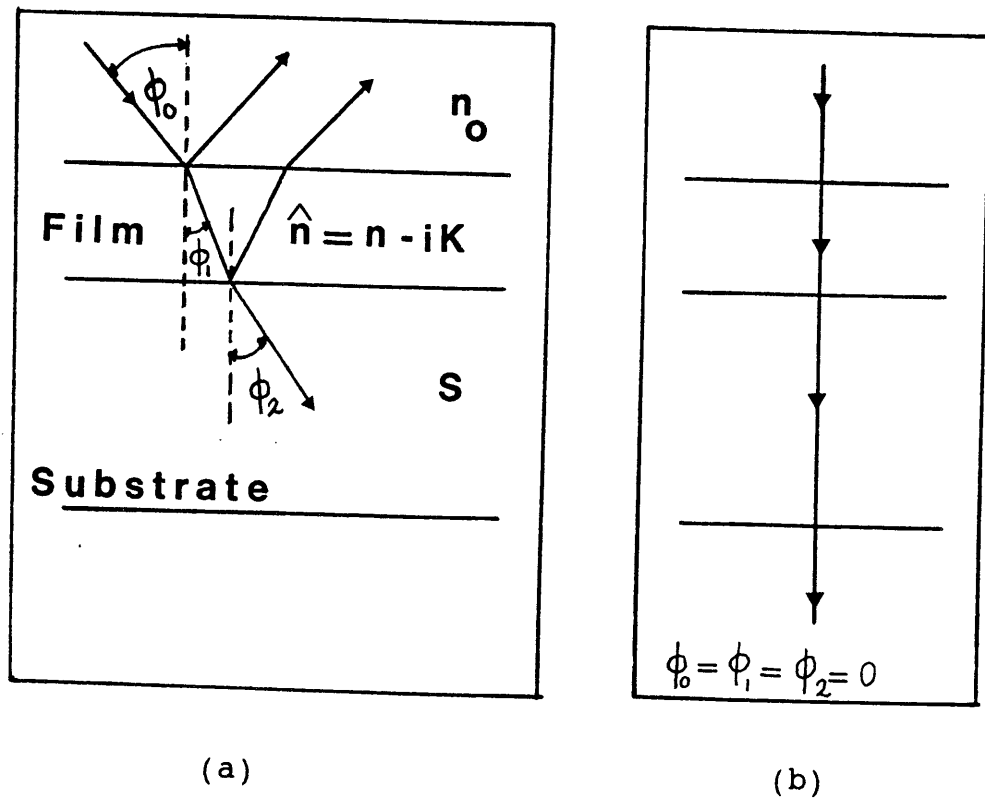


Fig.2.4 : Geometry for interference in a thin film on a transparent substrate. (a) multiple reflections at the film-substrate and film-air interfaces (b) practical situation; film-substrate composite is placed normal to the incident beam.

Assuming that a wave is incident on the film at an angle of incidence ϕ_0 , part of it will be reflected back and part will be refracted in the film with angle ϕ_1 . The refracted wave inside the film subsequently suffers

multiple internal reflections at the film-substrate and film-air interfaces. Each time an internal reflection takes place at the film-substrate interface, a partial wave is refracted into the substrate medium with an angle ϕ_2 . Rigorous analysis of the multiple reflections and transmissions at the interfaces shows that the total reflected amplitude R and the transmitted amplitude T must be expressed as a complex series. Swanepoel exploited these ideas taking into consideration a common spectroscopic situation whereby the film-substrate composite is placed normal to the incident beam (fig.2.4b). In this case $\phi_0 = \phi_1 = \phi_2 = 0$.

For reflection and transmission at the substrate without any film coating, the reflection coefficient R is given by

$$R = \left[\frac{S-1}{S+1} \right]^2 \quad (2.7)$$

and the transmission coefficient T_s by,

$$T_s = \frac{(1-R)^2}{1-R^2} \quad (2.8)$$

Substituting (2.7) into (2.8), gives

$$T_s = \frac{2S}{S^2+1} \quad (2.9)$$

or

$$S = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{\frac{1}{2}} \quad (2.10)$$

S can be determined using experimental value of T_s . In the wavelength region (600 nm to 1200 nm), the film-substrate system shows some weak absorption (about 20%), as a result of which transmission decreases slightly. Below 600 nm, transmission decreases rapidly destroying

the interference pattern. If the thickness is uniform, the transmission spectrum in the weakly absorbing region gives rise to interference fringes. Considering multiple reflections at various interfaces and in the limit $\alpha(\lambda)$ very weak, Swanepoel [1983] calculated the refractive index $n(\lambda)$ as,

$$n(\lambda) = \left[N + (N^2 - S^2)^{1/2} \right]^{1/2} \quad (2.11)$$

where

$$N = 2S \frac{T_M - T_m}{T_M T_m} + \frac{S^2 + 1}{2}$$

Here, T_M and T_m are the values of the transmission maximum and corresponding minimum at specific wavelength λ according to fig.2.5. This figure shows the transmission spectrum for a 30 at.wt.% Cu-70 at.wt.% GeO_2 film on a Corning 7059 glass substrate. The spectrum was obtained at normal incidence in the wavelength region 500 nm to 2000 nm using a CARY 2300 spectrophotometer. First, the transmission spectrum (T_s) of the substrate was obtained. It shows an interference-free pattern in the visible region. T_s was found to be about 93% from which the refractive index S was calculated using equation (2.10) to be 1.51. Corning 7059 glasses are known to have a refractive index of 1.52. Thus, the agreement is striking. For transmission through the film substrate-composite, a blank Corning 7059 glass substrate was used as a reference to eliminate the effect of substrate absorption. For the purpose of determining T_M , T_m and the corresponding refractive indices, an envelope to the maxima and minima was created. T_M and T_m were found at different wavelengths. Then, using eqn. (2.11), the values of $n(\lambda)$ were calculated to lie in the range 2.29 to 2.39. Knowing the values of n_1 and n_2 at two adjacent maxima or minima at λ_1 and λ_2 , the value of thickness was calculated using the standard expression [Jenkins et al. 1976],

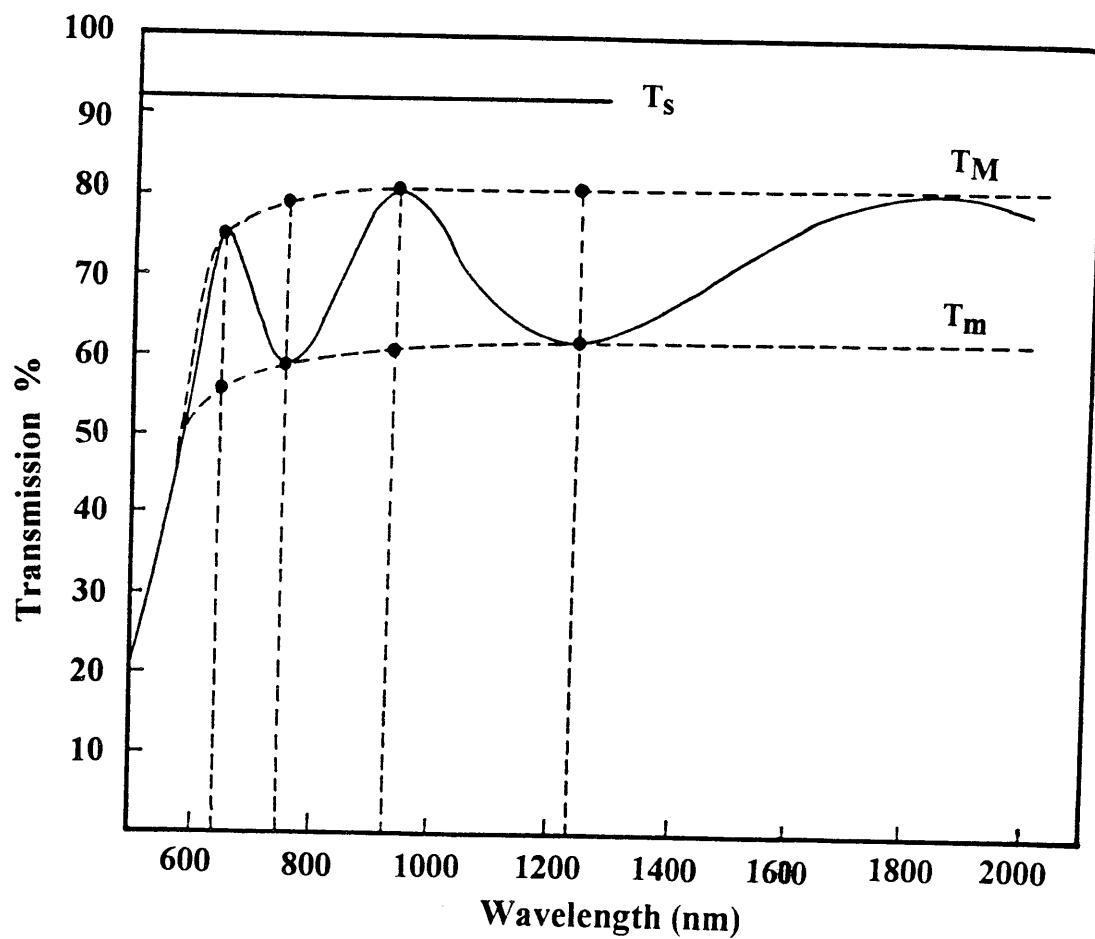


Fig. 2.5 : Transmission spectra for sample C (407 nm) on Corning 7059 glass substrate with transmission T_s . Curves T_M and T_m are according to text.

$$t = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (2.12)$$

Table 2.1 shows some typical values of T_M , T_m , n and thickness t at particular wavelengths λ . The mean value of the thickness calculated from the two sets of readings was found to be 403 nm. Thickness of the same film was measured in-situ with Edward's FTM5 thickness monitor as 411 nm. This is listed in table 2.1. As can be seen, a slight dispersion in the values exist, the uncertainty being about 2%. The best value of the thickness was obtained as the average of these two values, viz. 407 nm.

Table 2.1 Values of λ , T_M , T_m , n and t calculated from the spectrum of fig. 2.5

λ (nm)	T_M	T_m	n	t (nm)	Av t (nm)	t_{FTM5} (nm)	Mean t (nm)
1220	0.805	0.608	2.29	404	403	411	407
740	0.78	0.59	2.31	404			
950	0.80	0.60	2.31	402			
650	0.76	0.56	2.39	402			

In conclusion, it is seen that transmission interference effects gives rise to a spectrum from which refractive index and the thickness can be calculated simultaneously with remarkable accuracy. It is this advantage which has led many authors to use this technique; the accuracy is ± 1 to 2% [Hammam et al. 1986, Marquez et al. 1992, Al-Saie et al. 1993]. It must be mentioned that the accuracy to which n and t can be determined depends on the accuracy to which λ , T_M and T_m can be measured. The scale used for λ yields an accuracy of ± 5 nm and the maximum accuracy with which the CARY 2300 spectrophotometer

measured T_M and T_m is around ± 0.005 . Around 100 samples were prepared for the studies of electrical and optical properties. In each case, thickness was monitored in-situ and later on confirmed by using transmission technique as outlined in this chapter. A mean uncertainty of about ± 2 to 20 % was found between these two measurements.

Furthermore, in the strong absorption region ($\lambda \leq 600$ nm), the interference fringes vanish and the Swanepoel technique is unable to determine the refractive index. A knowledge of $n(\lambda)$ and the extinction coefficient $K(\lambda)$ in this region is essential for bandgap studies; this has been dealt with in some details in section (3.5.3).

OPTICAL PROPERTIES

3.1 Introduction

In recent years considerable interest has been developed in the study of optical properties of thin films due to their importance in optical and optoelectronic devices [Redfield 1963, Tauc et al. 1966, Dexter 1967, Dow et al. 1969, Davis et al. 1970, Stuke 1970, Morris et al. 1971, Moridi et al. 1977, Skettrup 1978, Dunstan 1982, Hogarth et al. 1981, Al-Ani et al. 1984, 1985; Ohring 1992]. Among the important issues concerning optical properties are the magnitude of refractive index $n(\lambda)$, the extinction coefficient $K(\lambda)$, the spectral range of transmission and absorption. Dielectric thin film, which consists of more than one component, possesses widely varying $\alpha(\lambda)$, $n(\lambda)$ and $K(\lambda)$ depending on the thickness and composition. As a result, this material is frequently used for fabricating modern optical devices (see section (1.1)). $n(\lambda)$ is basically the only optical constant of interest as far as optical coating is concerned. Dielectric materials employed in optical coating applications include fluorides (e.g. MgF_2 , CeF_3), oxides (e.g. Al_2O_3 , TiO_2 , SiO_2) and sulfides (e.g. ZnS , CdS) [Ritter 1975, Ohring 1992]. Generally, $n(\lambda)$ in fluoride and oxide films has a value in the range $1 \leq n \leq 2$ in the visible region. For many industrial applications, however, it is important to have materials with higher refractive index (>2) and transmittance ($>80\%$). For these reasons, materials such as sulfides and cermet films are commonly used in modern optical devices.

A few cermet systems with various metal and dielectric compositions, such as Cr-SiO [Milgram et al. 1968, Glang

et al. 1967], W-Al₂O₃ [Sichel et al. 1982], Mn-SiO [Al-Ani et al. 1985], Cu-GeO₂ [Al-Saie et al. 1993] and Cu-SiO [Khan et al. 1994] have been studied. A variety of common features emerge from these studies. Amorphous semiconducting materials generally exhibit absorption edges which are less abrupt and well-defined than corresponding crystalline form. The main features of the absorption spectra remain broadly similar e.g. a power law expression of the form $\alpha(\omega) \propto (\hbar\omega - E_{opt})^n$ in the high energy region ($\alpha(\nu) \geq 10^4 \text{ cm}^{-1}$) and a defect-induced tail at the lowest energy region ($\alpha(\nu) < 10^4 \text{ cm}^{-1}$). Furthermore, the exponent n is found to lie in the range 0.5 to 3, depending on whether the transition is allowed or forbidden. Most importantly, the main features of the absorption spectra are essentially preserved at the transition to the crystalline phase. In the high energy region, optical transitions conserve energy but not the wave vector K and the density of states near the band extrema has the same energy dependence in both crystalline and non-crystalline materials. Another important common feature is that for most amorphous materials, the band gaps often lie in the range 1-3 eV [Stuke 1970, Elliot 1990].

The origin of power law and exponential regions has been and continues to be controversial. Some causes of this controversy, resulting from our present inadequate knowledge of electronic structure and how it is effected by impurities and defects, have been discussed in sections (1.1.2) and (1.1.3).

In order to understand the optical behaviour of films, one must become familiar with the optical constants, their origin, magnitudes, and how they are effected by deposition parameters. In the following sections, these issues are first discussd within the context of current theoretical models. In addition, experimental

investigations which were carried out on Cu-GeO₂ thin films and their results are presented.

3.2 Optical absorption : The power law region

In optical absorption, two types of transitions must be distinguished: direct and indirect. In direct transitions, the band structure has a minimum in the conduction band and a maximum in the valence band for the same value of the wave vector K , i.e. $K=0$. This is shown in fig. 3.1a. The second type involves band structures where the valence band maximum occurs at different value of K than its conduction band minimum. In this case, the transition occurs through virtual states requiring some changes in K . This situation is shown in Fig. 3.1b.

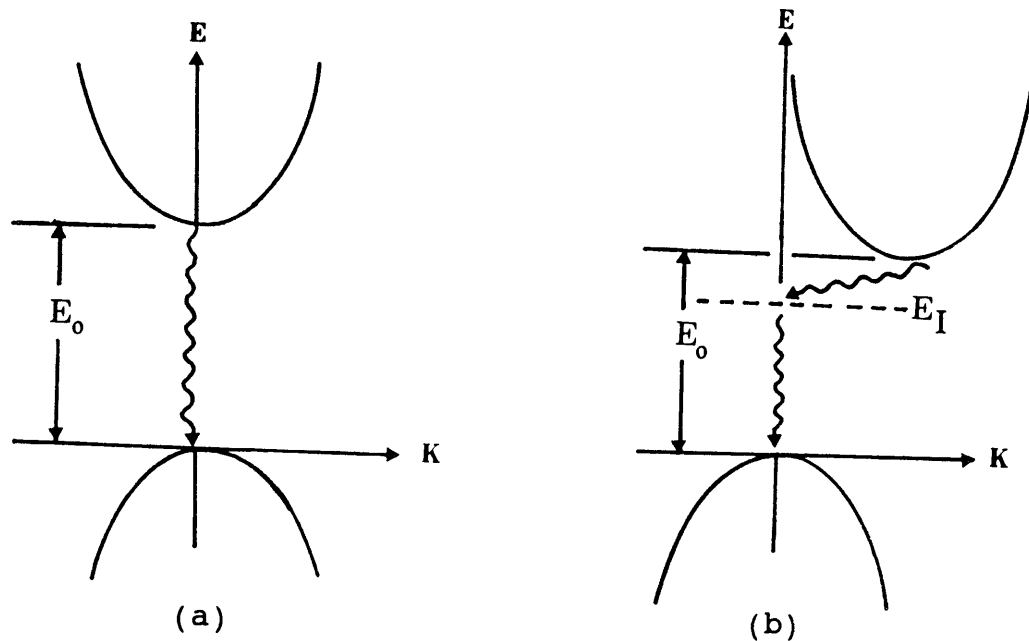


Fig. 3.1 (a) direct transition : an electron in the conduction band falls to an empty state in the valence band giving off energy (E_0) as a photon. (b) Indirect transition: transition takes place via a defect level (E_I) in which energy is not conserved. For the overall transition, however, energy is conserved and is given up as heat to the lattice rather than as an emitted photon.

To derive expressions for the absorption coefficient $\alpha(\nu)$ for direct and indirect transitions, we follow the approach of Elliot [1990], which is based on Tauc's [1966] work. Let the valence and conduction states be denoted by the Dirac state vectors $|i\rangle$ and $|f\rangle$, respectively, in Hilbert space. If H is the Hamiltonian operator of the system, then the energy eigen values of the valence bands (E_i) and the conduction band (E_f) can be obtained from the following eigen value equations,

$$H|i\rangle = E_i|i\rangle \quad (3.1a)$$

and

$$H|f\rangle = E_f|f\rangle \quad (3.1b)$$

The optical properties of crystalline and non-crystalline materials are deduced almost entirely from the one electron-expression for the imaginary component of the dielectric constant $\epsilon''(\omega)$, given by [Connell 1979, Elliot 1990],

$$\epsilon''(\omega) = \frac{2}{V} \left(\frac{2\pi e}{m\omega} \right)^2 \sum_i \sum_f |\langle f | \underline{P}(\omega) | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.2)$$

where V is the sample volume, $\underline{P}$ is the momentum vector and the summations are over all initial valence and final conduction states. The term $|\langle f | \underline{P}(\omega) | i \rangle|^2$ represents the transition amplitude (i.e. probability of transitions) between initial and final states. The Dirac δ function ensures that in vertical transitions, the overall momentum and energy remain conserved. Equation (3.2) can be written as,

$$\epsilon''(\omega) = \frac{2}{V} \left(\frac{2\pi e}{m\omega} \right)^2 |\underline{P}_{if}(\omega)|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.3)$$

where

$$|\underline{P}_{if}(\omega)|^2 = |\langle f | \underline{P}(\omega) | i \rangle|^2$$

$\underline{P}_{if}(\omega)$ represents the momentum transition matrix between final and initial states. The wave functions in the valence and conduction bands are Bloch functions which can be expanded in terms of a set of orthonormal localized state vectors $|nv\rangle$ and $|nc\rangle$ in the Hilbert space e.g.,

$$|i\rangle = V^{-1/2} U_K(r) e^{iKr} = \sum_n a_{inv} |nv\rangle \quad (3.4a)$$

and

$$|f\rangle = V^{-1/2} U_{K'}(r) e^{iK'r} = \sum_n a_{fnc} |nc\rangle \quad (3.4b)$$

For a crystal a 's are the plane waves representing the term e^{iKr} , and $|nv\rangle$ and $|nc\rangle$ are Dirac states in valence and conduction bands, respectively centered on different atoms n . The matrix element $\underline{P}_{if}$ can be evaluated for transition between delocalized to delocalized states as follows,

$$\begin{aligned} |\underline{P}_{if}(\omega)|^2 &= |\langle f | \underline{P}(\omega) | i \rangle|^2 \\ &= \langle f | \underline{P}(\omega) | i \rangle \langle i | \underline{P}^* | f \rangle \\ &= \sum_n |\langle nc | \underline{P}(\omega) | nv \rangle|^2 a_{inv} a_{inc}^* \end{aligned} \quad (3.5)$$

Normalization of Dirac initial and final states vectors yields,

$$a_{inv} a_{inc}^* = \frac{a^3}{V} \quad (3.6)$$

Therefore, equation (3.5) becomes,

$$|\underline{P}_{if}(\omega)|^2 = \frac{a^3}{V} \sum_n |\langle nc | \underline{P}(\omega) | nv \rangle|^2 \quad (3.7)$$

Here a is the inter atomic spacing. Substituting equation (3.7) into equation (3.3), one obtains,

$$\varepsilon'(\omega) = \frac{2}{V} \left(\frac{2\pi e}{m\omega} \right)^2 \frac{a^3}{V} \sum_n \left| \langle nc | P(\omega) | nv \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.8)$$

Now the density of states in both crystalline and amorphous materials is given by [Elliot 1990]

$$g(E) = \frac{1}{V} \sum_n \delta(E - E_n) \quad (3.9)$$

where $g(E)$ is the one-electron density of states per unit volume per unit energy. The density of states over the entire energy gap is given by,

$$N(E) = \int g(E) dE = \int \frac{1}{V} \delta(E - E_n) dE \quad (3.10)$$

For direct transitions, when the energy of the top of the valence band edge is taken to be zero, equation (3.9) yields,

$$\delta(E - E_n) = Vg(E)$$

or

$$\delta(E_f - E) = Vg_f(-E)$$

or

$$\delta(E - E_i - \hbar\omega) = Vg_i(E - \hbar\omega) \quad 3.11)$$

Equation (3.8) can now be rewritten as,

$$\varepsilon'(\omega) = 2 \left(\frac{2\pi e}{m\omega} \right)^2 a^3 \sum_n \left| \langle nc | P(\omega) | nv \rangle \right|^2 dE g_f(-E) g_i(E - \hbar\omega)$$

$$\text{or} \quad \varepsilon'(\omega) = 2 \left(\frac{2\pi e}{m\omega} \right)^2 a^3 \sum_n \left| \langle nc | P(\omega) | nv \rangle \right|^2 dE g_f(E) g_i(\hbar\omega - E) \quad (3.12)$$

Equation (3.12) suggests that $\varepsilon'(\omega)$ can be determined if the density of states in the valence and conduction bands

for which energy is conserved are known. It is generally assumed that the density of states above and below the conduction and valence band mobility edges can be represented, respectively, by the following power laws [Connell 1979, Elliot 1990],

$$g_i(E_n) \propto E_n^p \quad (3.13a)$$

and
$$g_f(E_p) \propto E_p^q \quad (3.13b)$$

Here E_n and E_p represent electron and hole energies in the respective bands. E_0 is the energy gap between conduction and valence band mobility edges. Inserting equation (3.13a and 3.13b) into equation (3.12), and noting that $E_p + E_n + E_0 = \hbar\omega$, one obtains,

$$\omega^2 \varepsilon''(\omega) \approx (\hbar\omega - E_0)^{p+q+1} \quad (3.14)$$

or
$$\alpha(\omega) \approx (\hbar\omega - E_0)^{p+q+1} \approx (\hbar\omega - E_0)^n \quad (3.15)$$

where $\omega^2 \varepsilon''(\omega) \approx \omega \alpha(\omega)$ (see section (3.4.5) for details) and $n = p + q + 1$.

Assuming a parabolic shape for the density of states at the band edges [Connell 1979, Mott et al. 1979, Elliot 1990] i.e. $p=q=1/2$, equation (3.15) becomes,

$$\alpha(\omega) \propto (\hbar\omega - E_0)^2 \quad (3.16)$$

The form of the absorption coefficient expressed by equation (3.16) has been observed experimentally for many amorphous materials since the initial work of Tauc et al. [1966] on a:Ge. However, it is not clear if E_0 represents the true value of the mobility edge-to-mobility edge optical gap. This uncertainty arises because equation (3.16) is satisfied for both delocalized to delocalized, and for localized to delocalized transitions. For

example, if a band of localized states exists above the valence band edge (E_V) with energy level, E_I say, then transitions from these states to the edge of conduction band (E_C) will also be given by the equation (3.16). Fig. 3.2 depicts this picture where a transition takes place from the top of the localized impurity states to the edge of the conduction band. In this case, the optical gap E_O or E_{opt} will be given by the difference between the conduction edge and the impurity level energy levels i.e. $E_O = E_{opt} = E_C - E_I$, in contrast to the mobility edge to mobility edge energy gap. Experimental determination of $\alpha(\omega)$ and E_O are necessary to resolve this uncertainty. Generally, for extended states to extended states transitions $\alpha(\omega)$ is larger in magnitude leading to higher value of E_O . For localized to extended state transitions, $\alpha(\omega)$ is relatively smaller corresponding to a diminished optical gap.

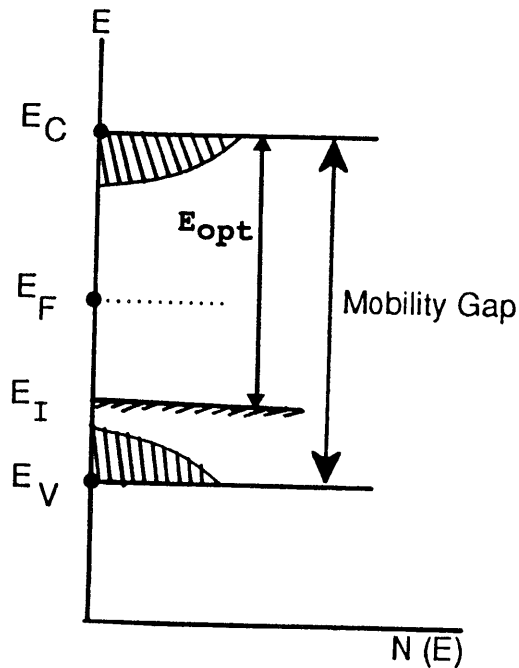


Fig.3.2 : Illustrating the Davis-Mott [1970] mobility gap model for an amorphous semiconductor. The hatched regions indicate the tails of localized states. The reduced E_{opt} is given by the difference $(E_C - E_I)$.

3.3 Exponential absorption region : The Urbach behaviour

Interband transitions embodied in equation (3.16) imply the existence of sharp optical absorption edges. In reality, however, a gradual increase in $\alpha(\omega)$ with photon energy has been observed in the lower energy region. This region shows an almost linear relation on a logarithmic scale. Such behaviour has been referred to in the literature as the Urbach behaviour [Urbach 1953]. This so called Urbach edge is found to have an exponential dependence on photon energy, given by

$$\alpha(\omega) = \alpha_0 e^{-\frac{\gamma(E_0 - \hbar\omega)}{kT}} = \alpha_0 e^{+\frac{(\hbar\omega - E_0)}{E_t}} \quad (3.17)$$

where $\frac{kT}{\gamma} = E_t$ is the width of the tail states. γ is a temperature-dependent parameter. Equation (3.17) implies that as temperature rises, the edge becomes broader, a behaviour which has been observed in many crystalline and non-crystalline materials (see section (1.1.3)). Though this seemingly universal behaviour points towards a common cause, no single explanation has been found satisfactory enough to explain its origin. Theoretical calculations tend to suggest that the exponential edge arises when the density of states in the tail states has the form $N(E) \approx \text{const.} e^{\beta E}$, where β is temperature-dependent given by $1/kT$ [Connell 1979]. This expression suggests a common origin for the Urbach edge if β can have a fairly constant value for all amorphous materials. However, a wide variety of experimental works [Tauc et al. 1966, Connell 1979, Tauc 1970, Mott et al. 1979, Elliot 1990] suggest that β is unlikely to remain invariant from material to material. This happens because the behaviour of transitions involving tail states are affected by impurities and defects.

An interesting experimental and theoretical challenge is to determine which, if any of the many mechanisms described in section (1.1.3), correctly accounts for the physical origin of the exponential behaviour in a particular material.

3.4 Experimental procedure

3.4.1 Film preparation

The film evaporation technique involving the electron beam gun has been described in section (2.2.3). For optical absorption studies, two sets of films were produced. The first set comprised films containing 30 at.wt% Cu and 70 at.wt% GeO₂. Appropriate mixes of the powders were first finely ground in a cleaned porcelain crucible and then pressed into thin disc shaped objects at a vacuum pressure of 8 tons for four minutes. They were then introduced in the evaporation chamber and heated to the melting point; a mechanical shutter covered the source. Once the entire disk had melted, heating was stopped and the compound allowed to cool. This step was performed in order to ensure uniform mixing of Cu and GeO₂ components. Films of varying thicknesses (227, 340 and 407 nm) were evaporated from a single graphite boat at a pressure of about 10^{-3} Pa on to ultrasonically cleaned Corning 7059 glass slides at a substrate temperature of 300 K.

The substrates were positioned centrally, relative to the source, and the films were deposited on to them at a beam voltage of 3 kV and a beam current of 10 to 12 mA, corresponding to deposition rates within the range 2 to 3.5 nm/s. The deposition rate and thickness were controlled by reflection interference of a He-Ne laser beam during the growth of the film using a photo-sensor,

which was then fed to a X-Y plotter via a lock-in amplifier. This technique has been discussed in some details in section (2.5.1). The Swanepoel technique (see section (2.5.3)) was employed to verify the thicknesses. The agreement between these two sets of measurements was within ± 10 to 15%. This uncertainty mostly arises from the uncertainty in the rate of deposition and the residual pressure in the vacuum chamber. A significant variation of residual chamber pressure with rising source temperature was noticed. As a result, the filament as well as the source were degassed for about 10 minutes prior to actual deposition. Consequently, an equilibrium condition (at 10^{-3} Pa) was reached within an uncertainty of 15 to 20%.

In order to study the effect of GeO_2 on the optical properties, a few films of 100 % GeO_2 , 395-410 nm thick, were evaporated at identical deposition conditions. Samples, marked A(227 nm), B(340 nm), C(407 nm) containing 30 at.wt.% Cu and D(395 nm, 100 % GeO_2), were used for thickness-dependent studies. The second set of films containing 5, 20 and 30 at.wt.% Cu, 410 nm thick, was evaporated under identical deposition condition for investigating composition-dependent properties.

Specimens for infrared absorption studies containing 5, 20, and 30 at.wt.% Cu, and 100% GeO_2 (all having identical thickness 410 nm) were evaporated on freshly cleaned and dried thin mono-crystalline silicon wafers doped with boron (thickness of wafers 0.012", resistance 15-25 ohms, Orientation $\langle 100 \rangle$). Prior to the evaporation, the silicon wafers were cut into appropriate dimension, cleaned in hydrofluoric acid for 2 minutes and then dried using a pressurized air jet. The films were introduced into infrared spectrometer (type Nicolet 5 DX) and measurements carried out at room temperature in the range 400 cm^{-1} to 4600 cm^{-1} . An uncoated silicon wafer

substrate was used as a reference to eliminate any possible influence of the substrate on the optical properties.

Fig. 3.3 shows the infrared absorption spectra for Cu-GeO₂ (lower curve) and 100% GeO₂ films (upper curve). No vibrational modes were observed in this range. Furthermore, spectra for all three Cu-GeO₂ samples coincide and are practically identical to that of the 100% GeO₂ film. This suggests that GeO₂ is the dominant matrix in the Cu-GeO₂ cermet system. Interestingly, the same conclusion has also been reached from DC conductivity (see Chapter 4) and Hall effect studies (see Chapter 5). Because GeO₂ is known to be an amorphous material, the identical spectra suggest that a Cu-GeO₂ film is also amorphous in nature. The absence of any vibrational mode in the spectra may be due to the fact that the films were too thick for the interference fringes to be resolved. Because IR studies in this range do not appear to furnish any information on the structural properties of the cermets, they will not be discussed further in this work.

3.4.2 Thermal stability and annealing measurements

The thermal stability of the films were studied using a Shimadzu DT-30 thermal analyzer to ensure that the annealing temperature was lower than the glass transition temperature T_g . The differential scanning calorimetry technique was applied. The DSC curve shown in fig. 3.4 was obtained at a heating rate of 20°C/min. It is clear that there is no single glass transition peak (T_g) up to 500°C. Therefore, the films were annealed at 250°C inside a Thermodyne (model 600) ashing furnace at atmosphere pressure for 2 hours. The specimens were then cooled to room temperature at a rate of 2°C/min.

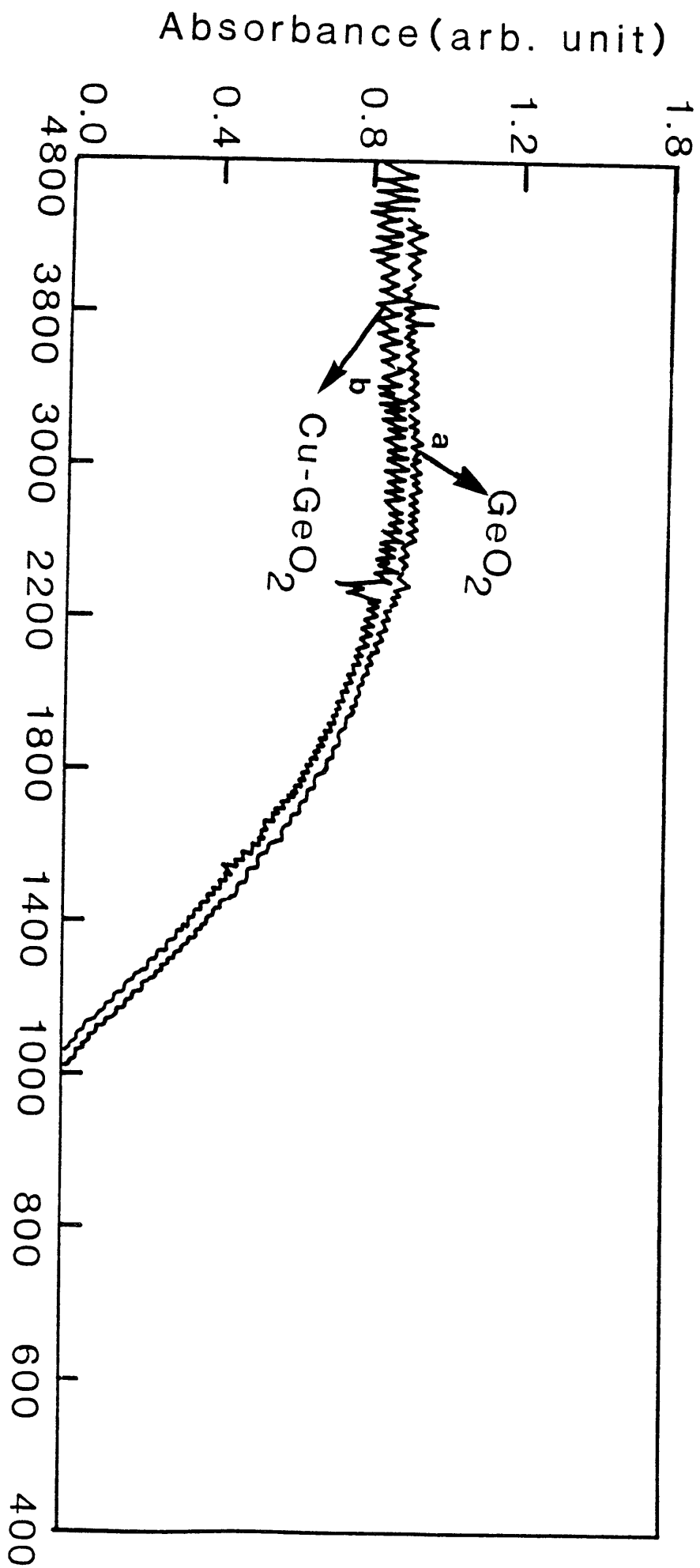


Fig.3.3 : Infrared absorption spectra of 410 nm thick (a) 100% GeO₂ film; (b) Cu-GeO₂ films containing 5 at.wt% Cu, 20 at.wt% Cu and 30 at.wt% Cu. Spectra for all three samples coincide.

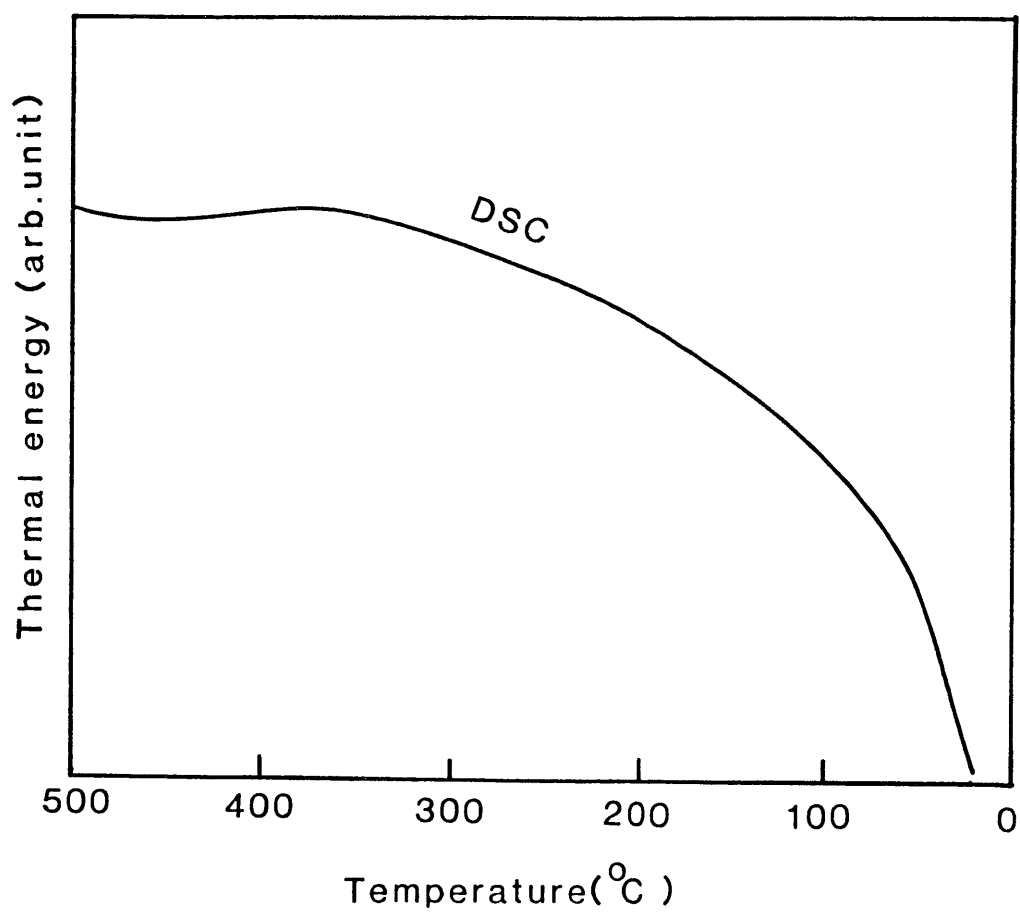


Fig. 3.4: DSC curve of the 30 at.wt.% Cu-70 at.wt.% GeO₂ cermet (in bulk form).

3.4.3 X-ray diffraction and fluorescence studies

X-ray diffraction and fluorescence measurements were performed on Cu-GeO₂ specimens using a Philips (model PW 1729) X-ray generator. With all the scans, a Corning 7059 glass substrate was used as a reference to eliminate the substrate influence. Fig. 3.5 shows the scans from 10° to 65° (2 θ) for samples 1 (5 at.wt% Cu), 2 (20 at.wt% Cu), 3 (30 at.wt.% Cu) and the Corning 7059 glass substrate. The top spectrum for sample 1 coincides with that of the substrate. The scan shows only diffusive diffraction rings indicative of an amorphous material. The spectra do not show any evidence of crystallinity on either fresh or annealed samples. A broad hump was noticed at 2 θ =23° for the glass substrate and sample 1. This was repeated for the other two samples in a diminished form signifying that the glass base is observed. The X-ray fluorescent (XRF) study does not show any definite trend in the count rates. These are given in Table 3.1.

Table 3.1 XRF count rates for the samples 1 (5 at.wt.%Cu), 2 (20 at.wt.% Cu) and 3 (30 at.wt.% Cu)

Samples	GeK α (cps)	CuK α (cps)
1	340	460
2	332	469
3	333	437

The absence of a definite trend in the count rates may be due to the somewhat thinner nature of the films i.e. the thicknesses may be less than the 'escape depth'. It could also be indicative of the fact that the film thicknesses were not identical in the three samples for meaningful comparison. In fact DC conductivity results in Chapter 4

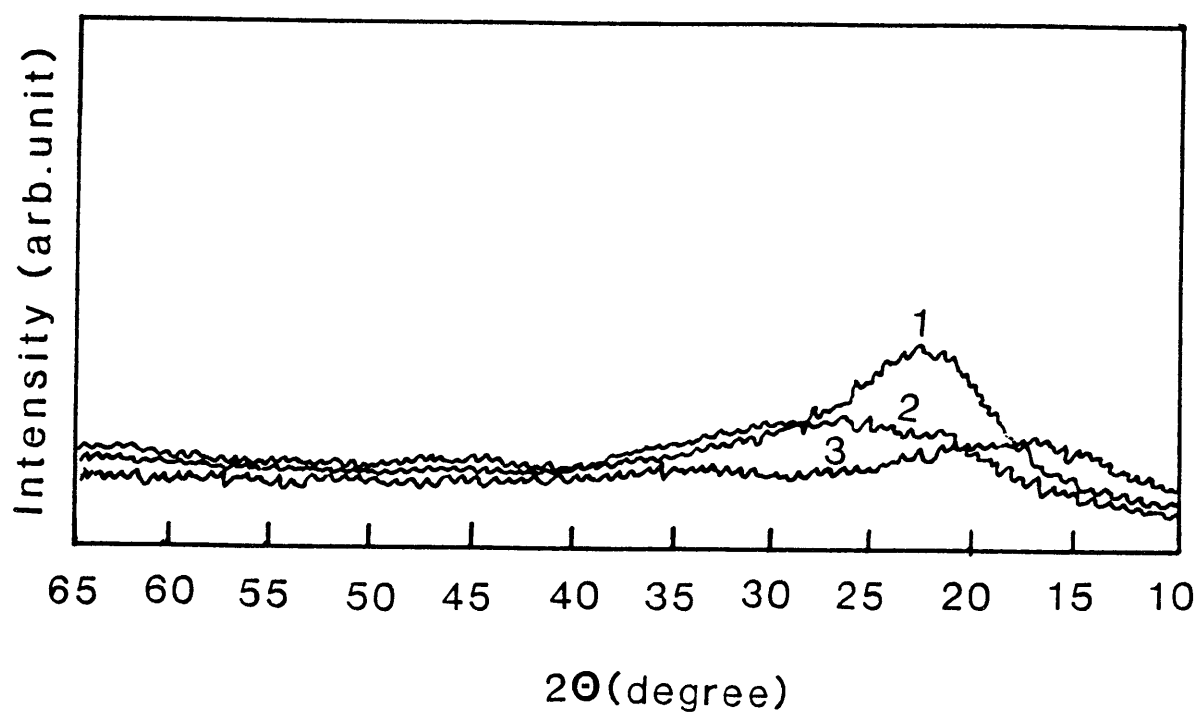


Fig. 3.5: X-ray diffraction spectra of (1) Corning 7059 glass substrate and 5 at.wt.% Cu film (410 nm); (2) 20 at.wt.% Cu film (410 nm); (3) 30 at.wt.% Cu film (410 nm).

do support this view and hence, XRF results will be discussed further in that chapter (section (4.2.3)).

The DSC studies (fig. 3.4) have shown that amorphous nature of the specimens persists with no evidence of a phase transition up to 500°C. XRD and IR studies, also, confirm the amorphous nature for both fresh and annealed (at 250°C) samples. Apart from establishing the amorphous nature of the films, DSC, IR and XRD studies have no further bearing on the present studies. Consequently, these results will not be discussed further in this work.

3.4.4 Spectroscopic measurements

Optical transmission measurements in the range of 550 to 2000 nm were carried out using a CARY 2300 double beam spectrophotometer with automatic data acquisition by a DS-15 desk-top computer (plate 2). Fig. 3.6 shows the block diagram of the transmission as well as the absorption measurement system. The system consists of four major components :

- (a) CARY 2300 UV-VIS-NIR spectrophotometer with IEEE interfaces. The system incorporates a microprocessor which enables one to preprogram and control the instrument through key board. Simultaneously, the system provides a continuous display of all relevant information on the monitor screen. The following are a few important specifications of this equipment.

Wavelength accuracy :	UV-VIS ± 0.20 nm
	NIR ± 0.80 nm

Absorbance range	:	-0.300 to 4.5
Transmission range	:	0 to 200.00
Temperature range	:	0 to 100.00°C
Wavelength range	:	185 to 3152 nm

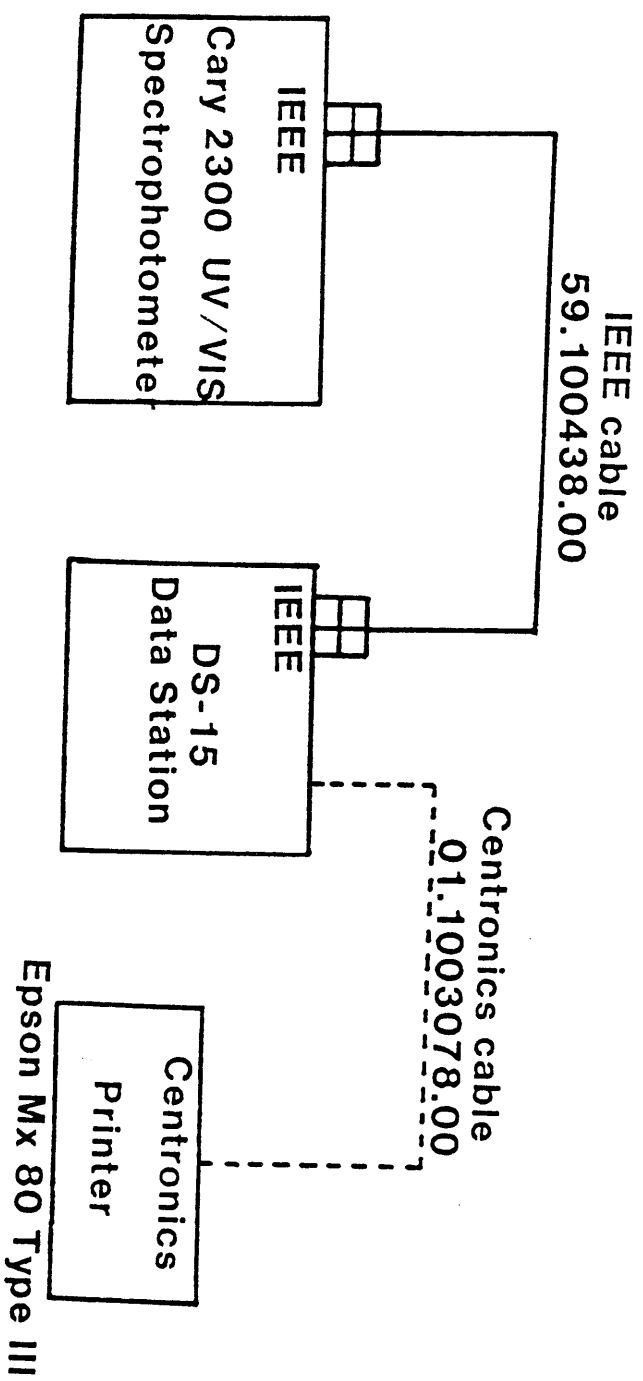


Fig.3.6 : Block diagram of the spectroscopic measurement system.

- (b) VARIAN DS-15 Data acquisition station (i.e. the desk-top computer) with double-sided drives and IEEE interface and cable
- (c) CARY 2300 DS-15 multiscan program
- (d) Printer with centronic interface and a centronic cable

The VARIAN DS-15 data station supported by the multiscan program allows full automated control of optical transmission and absorption spectra. The data are stored at selectable intervals of 0.05, 0.2, 1.0, or 5.0 nm. The software is used on-line with the CARY 2300 spectrophotometer for spectral calculations and report generation.

The optical absorption measurements in the range 270-800 nm were carried out for both unannealed and annealed films. A Corning 7059 glass slide was used as a reference to eliminate the effect of substrate absorption. The absorption coefficient $\alpha(\nu)$ was obtained using the standard relation,

$$\alpha(\nu) = \frac{1}{t} \ln A \quad (3.18)$$

where A is the absorbance of the films recorded by the DS-15 data station and t is the thickness of the films.

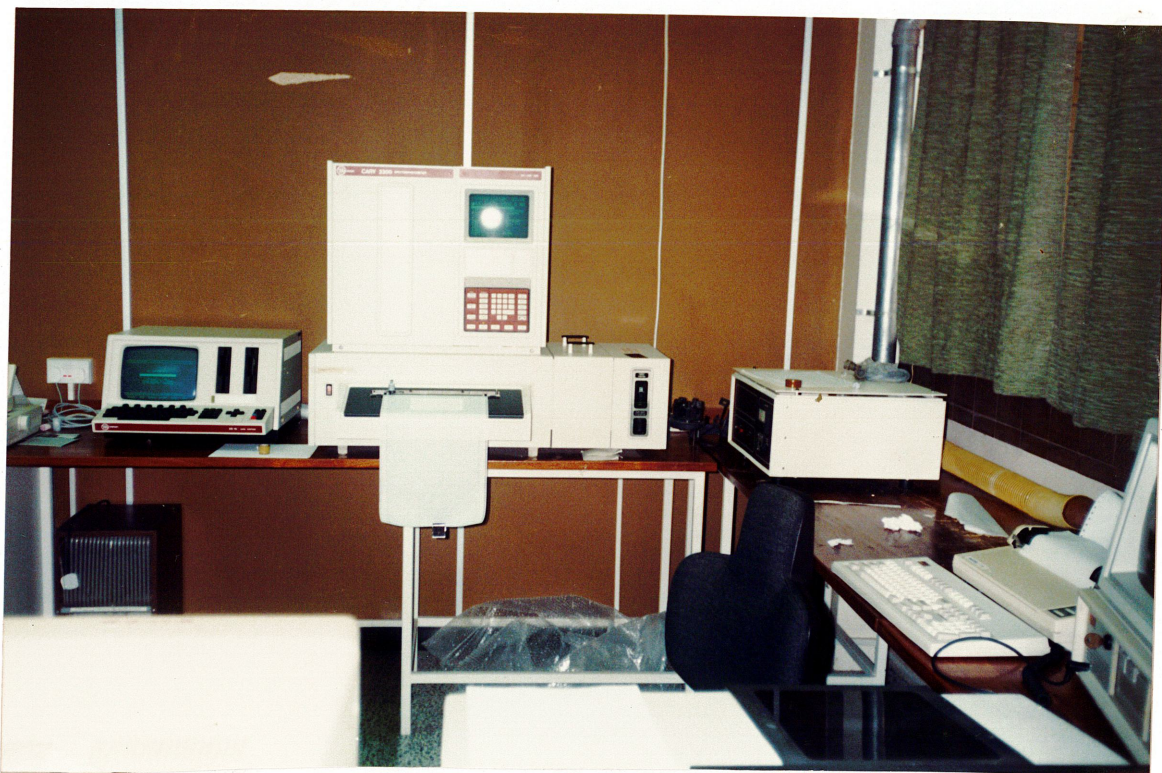


Plate 2 : Optical transmission and absorption measurements system (e.g. CARY 2300 UV-VIS-NIR spectrophotometer and VARIAN DS-15 Data acquisition station)

3.4.5 Determination of refractive index and extinction coefficient

The complex refractive index $\hat{n}(\lambda)$ and the complex permittivity $\hat{\epsilon}$ of amorphous and crystalline semiconductors are frequently used to describe the optical properties. These are given by,

$$\hat{n}(\lambda) = n(\lambda) - iK(\lambda) \quad (3.19)$$

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) \quad (3.20)$$

where $n(\lambda)$ is the real part of the complex refractive index and $K(\lambda)$ is called the extinction coefficient. The real part of the permittivity $\epsilon'(\omega)$ is related to the

polarizability, and the imaginary part $\varepsilon''(\omega)$ to the optical absorption coefficient $\alpha(\omega)$. Either of the sets: (n, K) and $(\varepsilon', \varepsilon'')$ are called optical constants. In general, they are wavelength-dependent material properties. For a plane electromagnetic wave of frequency ν propagating through the films, classical electromagnetic theory gives the following simple relationship between these parameters,

$$\varepsilon'(\omega) = n^2 - K^2 \quad (3.21)$$

and
$$\varepsilon''(\omega) = 2nK \quad (3.22)$$

The extinction coefficient $K(\lambda)$ is related to the absorption coefficient $\alpha(\lambda)$ by

$$K(\lambda) = \frac{\alpha(\lambda)\lambda}{4\pi} \quad (3.23)$$

Substituting equation (3.23) in equation (3.22), one obtains the relationship between $\varepsilon''(\omega)$ and $\alpha(\lambda)$ e.g.

$$\omega\varepsilon''(\omega) \approx \alpha(\omega) \quad (3.24)$$

The extinction coefficient $K(\lambda)$ was calculated from the known values of $\alpha(\lambda)$ using equation (3.23). The refractive index $n(\lambda)$ of the films were calculated from the transmission interference fringes employing the Swanepoel technique. Details of this technique and the transmission spectra of the sample C have been given in chapter 2 (see section (2.5.3)). The refractive index of the samples was found to vary between 2.31 to 2.39 in the wavelength range 900 nm to 600 nm.

3.5 Results and discussions

3.5.1 Thickness dependent Optical transmission and absorption

Fig. 3.7 shows the transmission spectra of a Corning 7059 glass substrate (marked G) and samples A, B and C at room temperature in the wavelength range 190-1000 nm. In the visible region (400-850 nm), G has about 93% transmittance but decreases rapidly in the UV region ($\lambda \leq 340$ nm). Sample A (227 nm) shows somewhat higher transmittance (about 95 %) in the visible region over all other samples, including the bare glass substrate. It is clear from this figure that transmittance decreases with increasing film thickness. Heat-treatment of the samples at 250°C for two hours at ambient temperature has a negligible effect on the transmittance. This is clearly seen from the absorption spectra of annealed films (fig. 3.9). No effort was made to heat-treat at higher temperatures for longer periods, for it was the intention of the author to study the optical and electrical properties of the cermets in amorphous state only.

Figs. 3.8 and 3.9 show the optical absorption spectra at different thicknesses for unannealed and annealed films, respectively. In fig. 3.8, the optical absorption edge, which is defined as the photon energy at which absorption starts increasing from zero, shifts towards higher wavelengths with increasing film thickness. This feature is generally retained for the annealed films, see fig. 3.9, although the absorption edges are seen to move towards higher wavelengths, leading to a decrease in the values of E_{opt} .

The absorption data shows that the onset of the higher absorption region occurs below the cut-off wavelengths

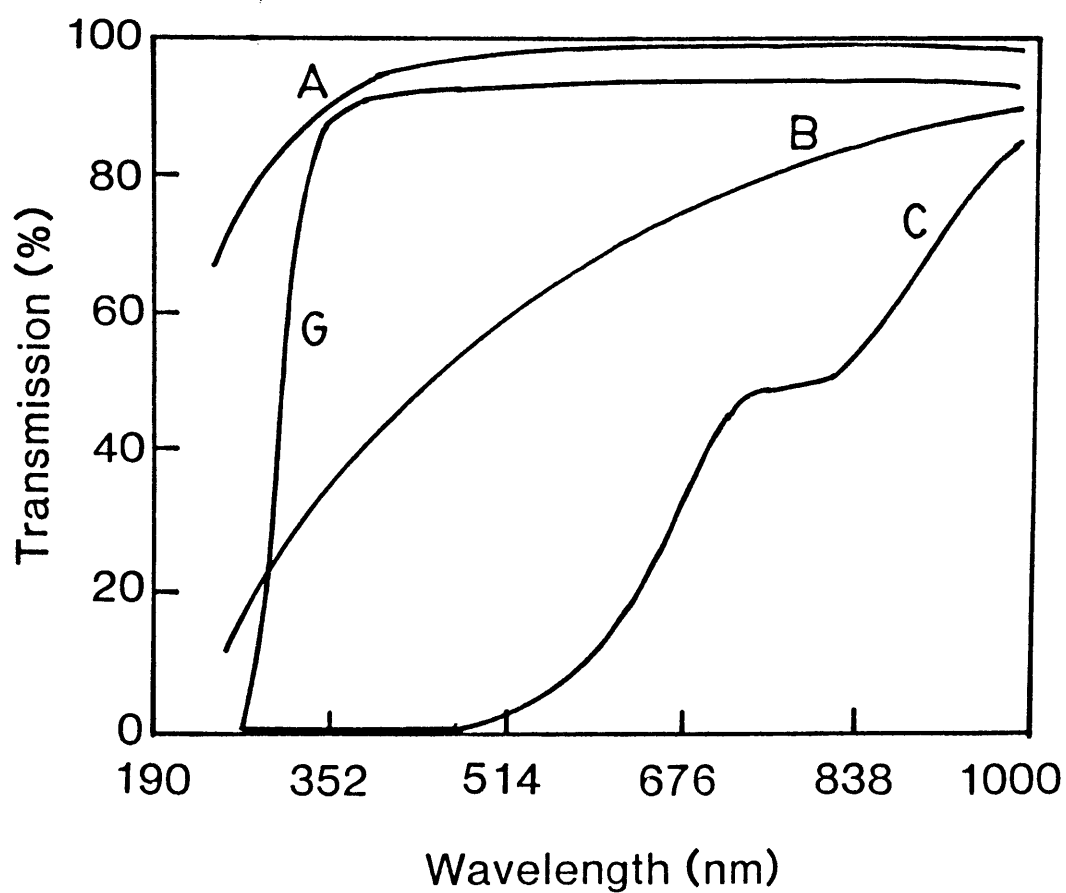


Fig.3.7: Transmission spectra of 30 at.wt.% Cu-70 at.wt.% GeO₂ films at different thicknesses and Corning 7059 glass substrate at room temperature in the range 190 to 1000 nm : (A) 227 nm, (B) 340 nm, (C) 407 nm, and (G) Glass substrate.

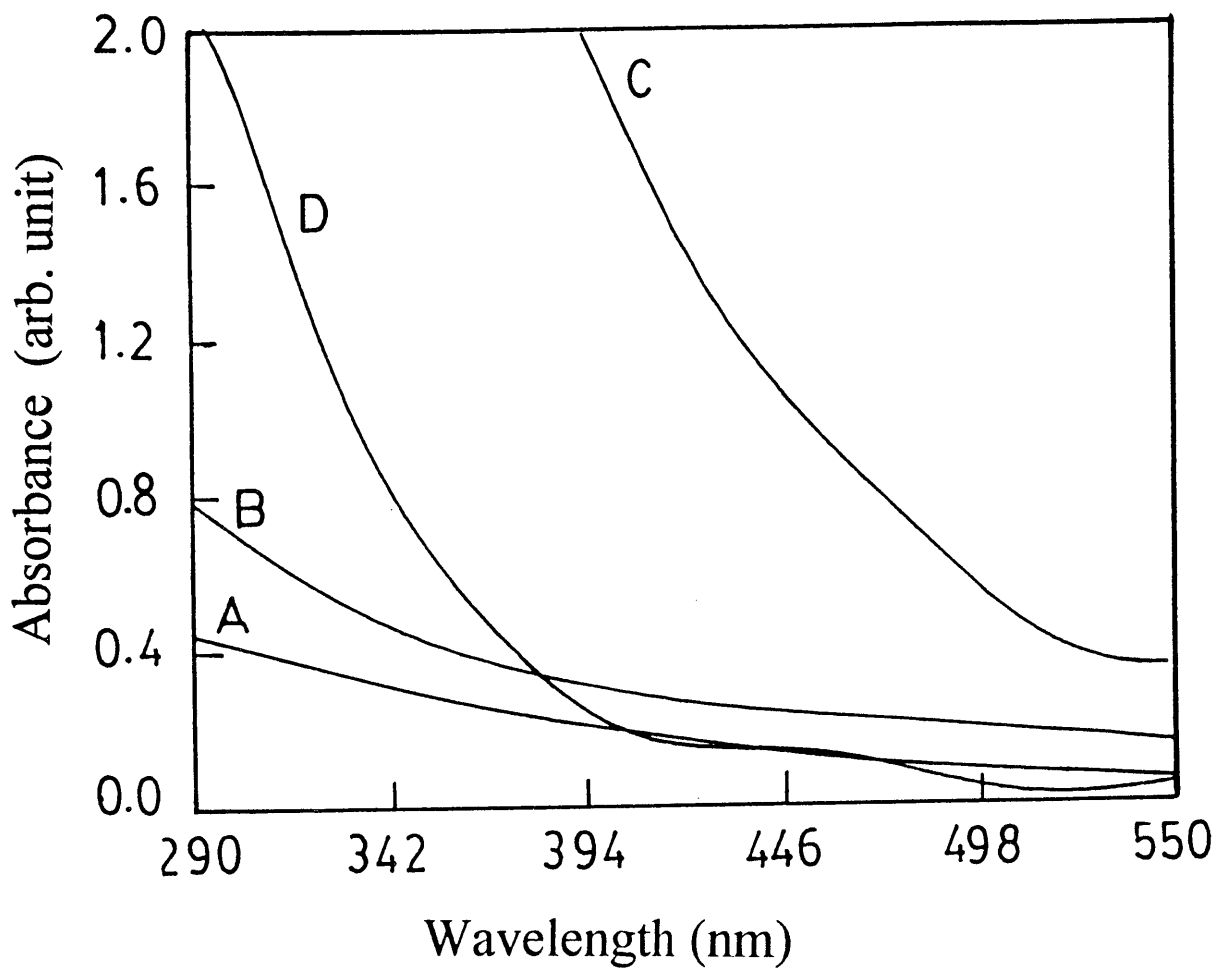


Fig.3.8: Absorption spectra for unannealed films as a function of wavelength : (A) 227 nm, (B) 340 nm, (C) 407 nm, and (D) 395 nm (GeO₂).

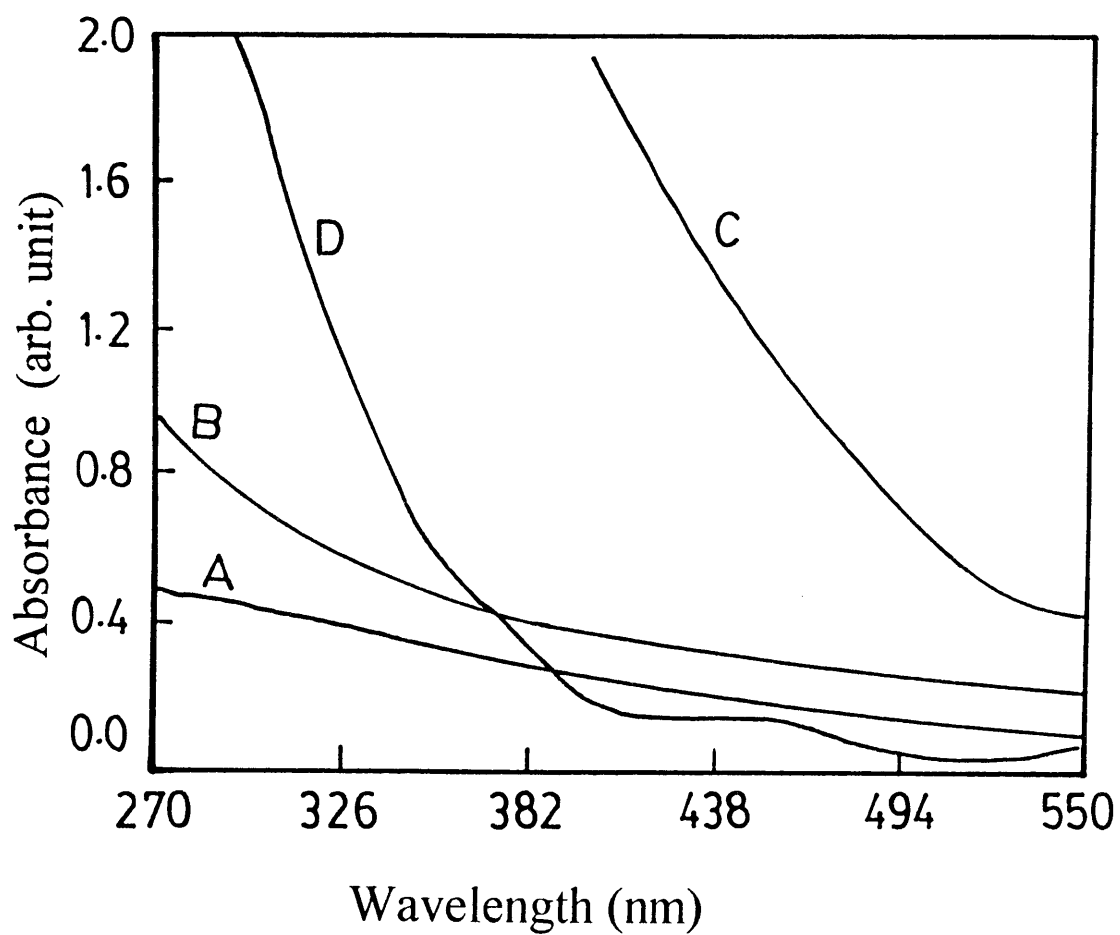


Fig.3.9: Absorption spectra for annealed films as a function of wavelength : (A) 227 nm, (B) 340 nm, (C) 407 nm, and (D) 395 nm (GeO_2).

400 nm for the samples A, and 500 nm for the samples B and C. These correspond to absorption coefficients: $\alpha(\nu) \geq 3.1 \times 10^6 \text{ m}^{-1}$ for sample C, $\geq 3.06 \times 10^6 \text{ m}^{-1}$ for B and $\geq 2.8 \times 10^6 \text{ m}^{-1}$ for sample A. These regions correspond to region 1 in fig. 1.1 and may be analyzed by plotting $(\alpha h\nu)^{1/2}$ against photon energy in accordance with equation (3.16). Figs. 3.10 and 3.11 show these plots for unannealed and annealed films, respectively. The graphs have well-defined linear regions which confirm that the cermet and GeO_2 films obey equation (3.16). Values of E_{opt} are obtained by extrapolating the linear portions. These values are listed in Table 3.2. For unannealed films, it is seen that E_{opt} systematically decreases with in the range 1.99 to 1.69 eV as the thickness of the films decreases from 407 nm to 227 nm. The same trend continues for annealed films but annealing has the effect of reducing the optical gap further.

Some explanations for the variation of E_{opt} with thickness are given by Al-Ani et al. [1984]. These authors contend that dangling bonds created during the deposition process might introduce some structural defects in the films. In turn these defects form localized states in the material. As film thickness increases, these defects and, hence, the localized states are reduced and the films become more homogeneous and amorphous. As a result E_{opt} increases. E_{opt} for 100% GeO_2 (395 nm) is estimated to be 2.80 eV whereas that for sample C (407 nm) is found to be 1.99 eV. Because these two films have almost equal thickness and have been produced under identical deposition conditions, it appears that the addition of Cu to the matrix of GeO_2 produces a reduction in E_{opt} . Similar observations have been made by other authors [Al-Ani et al. 1985] for the Mn-SiO system. It may be noted that for 100% GeO_2 glass E_{opt} has been reported to be 2.08 eV [Hogarth et al. 1981] and 3.75 eV [Khan et al. 1982]. For 100% SiO (852

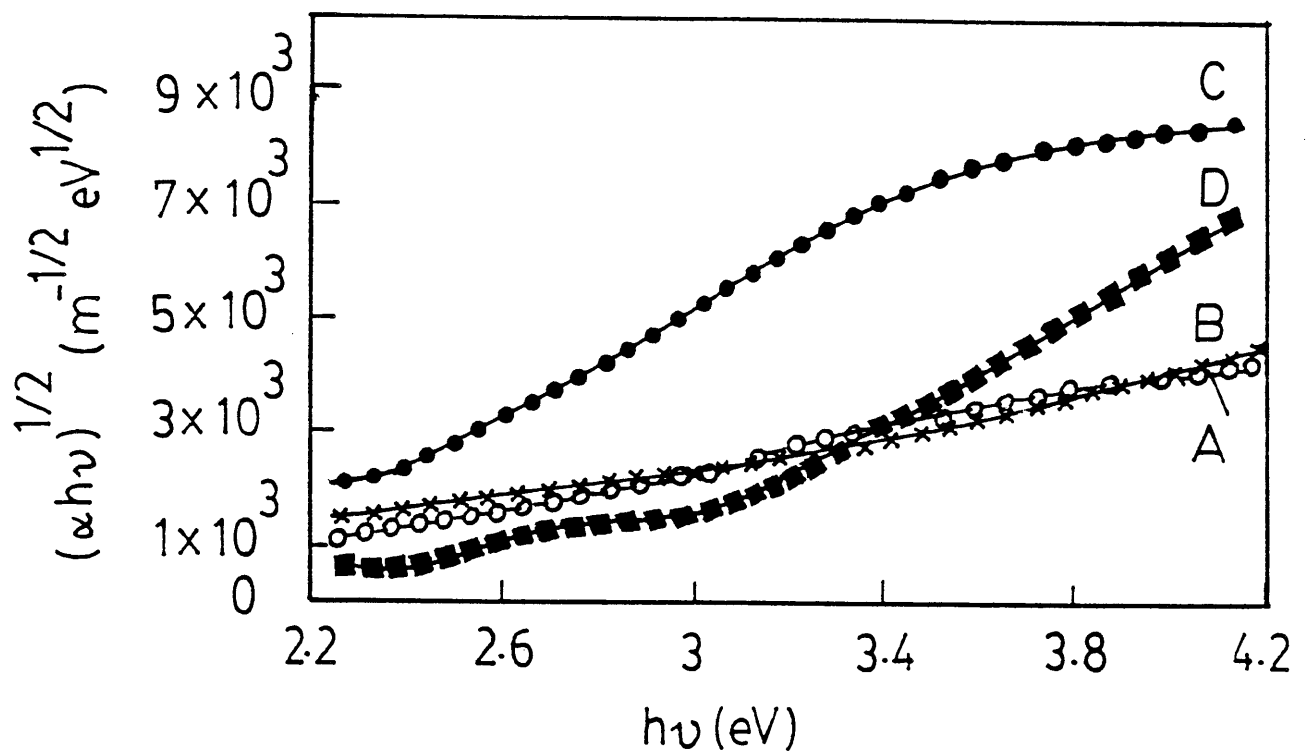


Fig.3.10: Optical absorption for unannealed films replotted in accordance with eqn.(3.16) : (A,B,C) Cu-GeO₂ cermet, and (D) amorphous GeO₂.

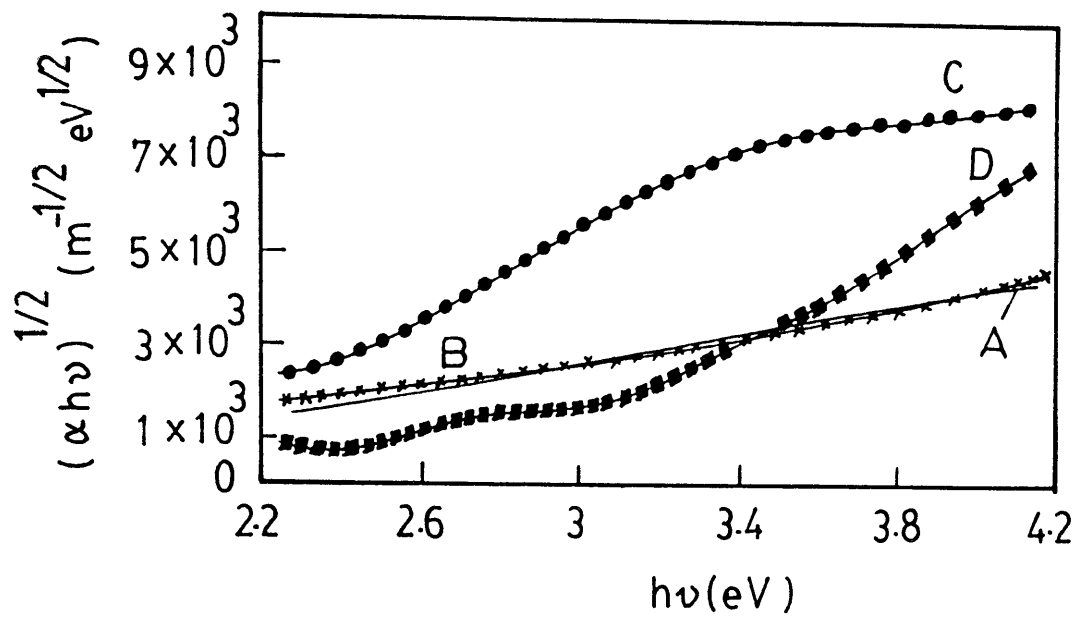


Fig. 3.11: Optical absorption for annealed films replotted in accordance with equation (3.16) : (A,B,C) Cu-GeO₂ cermets, and (D) amorphous GeO₂.

nm) thin films, Al-Ani et al. [1984] reports E_{opt} to be 2.73 eV for slow rates of evaporation.

Table 3.2 Optical properties of 30 at.wt% Cu- 70 at.wt.% GeO_2 cermet films deposited at a substrate temperature of 300 K and a vacuum pressure of 10^{-3} Pa

Films	Thickness t (nm)	Deposition rate R (nm/s)	Before annealing $E_{opt}(eV)$	Before annealing $E_e(eV)$	*After annealing $E_{opt}(eV)$
A	227	3.2	1.69	0.60	1.30
B	340	2.0	1.96	1.23	1.70
C	407	3.1	1.99	0.64	1.85
D(GeO_2)	395	3.5	2.80	-	2.86

* annealed at 250 °C (see section (3.4.2))

As seen from Table 3.2, the values of E_{opt} for annealed cermets are smaller than those for unannealed cermets, which is consistent with the shift of the absorption spectra towards higher wavelengths (fig. 3.9). This shift may be associated with a slight crystallization of the films during annealing resulting in a decrease in thickness. Consequently, the refractive index of the films increases, leading to an increase in optical-density. As is evident from figs. 3.10 and 3.11, the factor $(\alpha h\nu)^{1/2}$ increases as the film thickness increases, resulting in a higher transition probability of carriers across the optical gap [Choudhury et al. 1981].

Further support that an impurity band (formed by the localized states) does exist within the mobility gap, comes from the DC conductivity results (Chapter 4). It is shown there that since the thermal activation energy $E_a < (1/2) E_{opt}$, an impurity band must exist above the Fermi level. Therefore, as Davis et al. [1970] predicted, E_{opt} will not be a measure of the band-to-band energy gap. A diminished E_{opt} should be considered as the signature of optical transitions from the impurity band states (see fig. 3.2). Thus, depending on the nature and extent of these defect states incorporated during the deposition process, a particular material can exhibit different optical energy gaps at a particular temperature. This could be a possible reason why 100% amorphous GeO_2 thin films possess different E_{opt} e.g. 2.08 eV [Hogarth et al. 1981], 3.75 eV [Khan et al. 1982] and 2.80 eV [Al-Saie et al. 1993]. With regard to Cu- GeO_2 cermet, there are, unfortunately, no other published data which could be used for a comparison.

3.5.2 The Urbach behavior

The tail parts in figs. 3.8 and 3.9 may be regarded as the exponential absorption which corresponds to region 2 in fig. 1.1. For a better view, the general shape of the absorption edge of Cu- GeO_2 cermet is also shown in fig. 3.12. For each film it is seen that $\alpha(\nu)$ increases exponentially with $h\nu$ in certain regions suggesting that the Urbach rule (equation 3.17) is being followed. These regions are shown in the separate plots in fig. 3.13. The values of the band-tail width E_e are calculated from the slopes of these curves, and are listed in Table 3.2: the values lie in the range 0.60 to 1.23 eV for samples A, B and C. There does not appear to be any systematic dependence of E_e on thickness. The values of E_e are quite

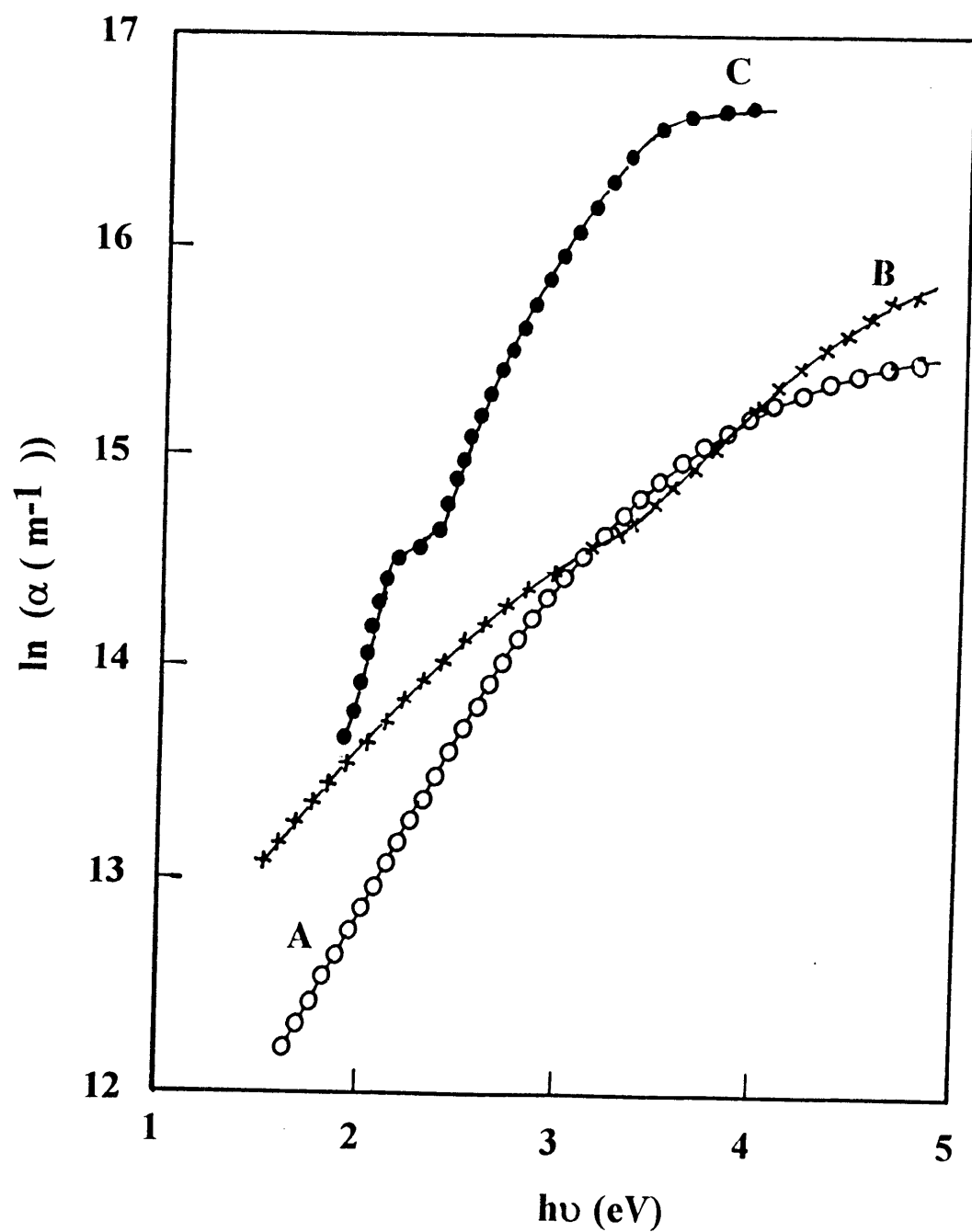


Fig.3.12 : General shape of the absorption edge of the cermet for film thicknesses : (A) 227 nm, (B) 340 nm, and (C) 407 nm.

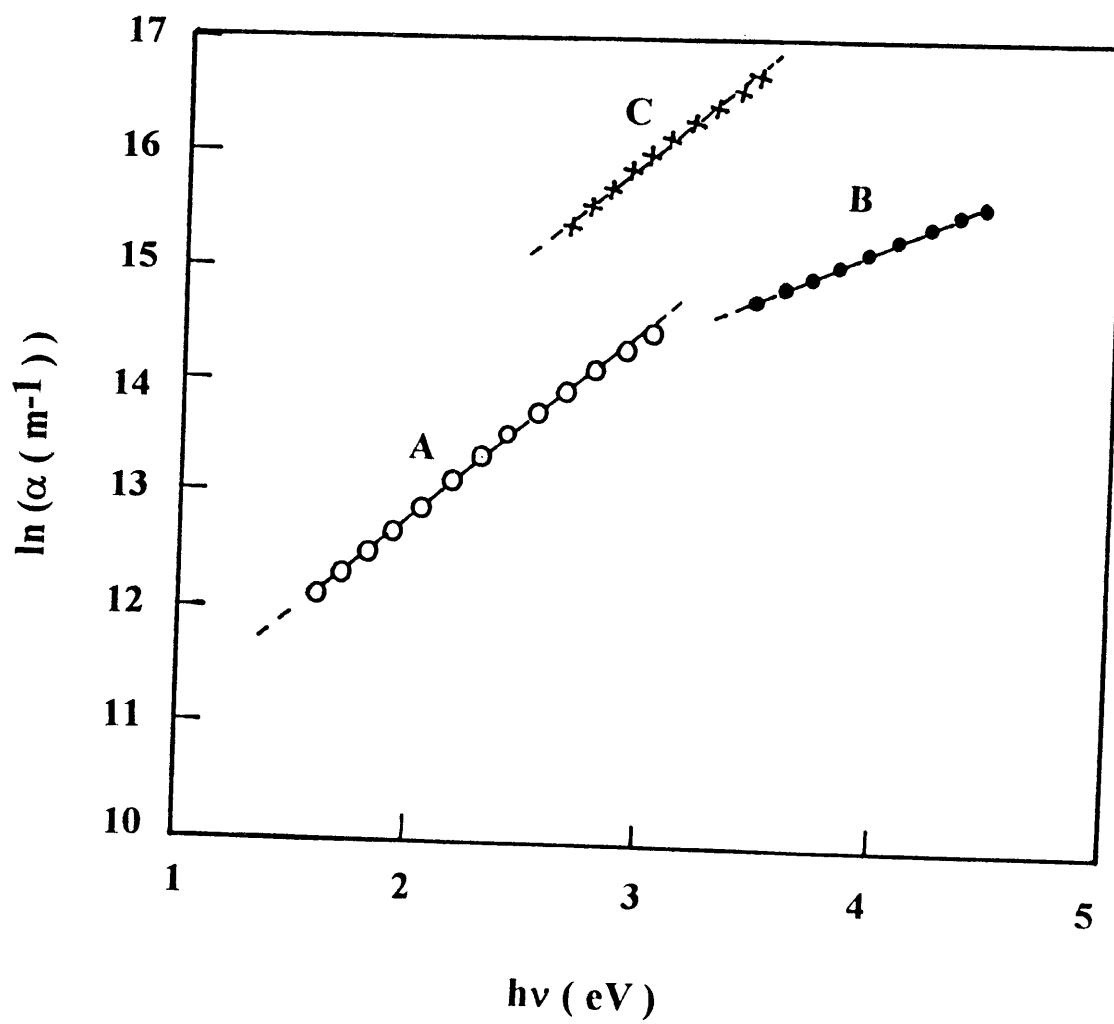


Fig.3.13 : Urbach behaviour of the absorption edge of the cermets A,B and C plotted in accordance with eqn.(3.17).

large compared to those for many amorphous semiconductors [Mott et al. 1979] but they are consistent with those of Mn-SiO₂ cermetes [Al-Ani et al. 1985]. These authors obtained E_e in the range 0.45 to 1.10 eV for different Mn concentrations. Moridi et al. [1977] found that E_e lay between 0.66 and 1.06 for various Cu concentrations in copper-calcium phosphate glasses.

We will now briefly discuss the causes of this exponential Urbach behaviour. It is generally believed that the Urbach tail is a disorder-induced phenomena near band edges. Two main reasons are attributed for this [Mott et al. 1979, Elliot 1990]. Either the behaviour arises from the exponential form of the density of states at the band edges or from a particular universal absorption mechanism. Dow et al. [1972] suggest that the behaviour arises from an electric field-induced broadening of an exciton line in localized states. They showed in explicit calculations that fluctuations in microfields associated with impurities will create new states in the forbidden gap. This scenario is closely related to the electron-impurity scattering process that results in lattice distortion and band-tail behaviour in amorphous materials. Tauc et al. [1966] proposed that this effect arises from electronic transitions between localized states near the band edges. The energy of transition will be smaller than the thermal-activation energy of intrinsic conductivity observed in many amorphous materials. From a rigorous analysis of optical transitions in a:Ge near band edges, they find that the density of localized states falls off exponentially below the onset of optical-gap energy. They further contend that since the density of localized states varies with composition and temperature, the band-tail width E_e should also vary as a function of these two parameters.

Davis et al. [1970] dispute Tauc's proposals on the ground that Urbach edges occur in many amorphous semiconductors with roughly similar slopes at room temperature. The temperature dependence of the slopes usually follow the equation (3.17) at higher temperatures, but at lower temperatures (when localization is predicted to occur) the slopes show a broadening proportional to $(kT)^{1/2}$ [Connally 1979]. The observed exponential edges in many amorphous semiconductors [Mott et al. 1979, Elliot 1990] suggest that the broadening is dominated by microfields associated with impurities in agreement with Dow-Redfield [1972] predictions.

In the present work, however, the values of E_g are found to vary significantly with thickness and compositions (see figs. 3.13 and 3.16). Furthermore, conductivity (Chapter 4) and Hall effect (Chapter 5) studies show that low temperature activation energies (0.10 to 0.25 eV) are considerably smaller than the high temperature activation energies (0.66 to 0.77 eV) and that the density of carriers in the localized states does follow an exponential behaviour. These observations lead us to believe that Urbach edges in Cu-GeO₂ thin cermet films arise from electronic transitions between localized states at the band-tails in agreement with Tauc's [1966] proposals.

3.5.3 Composition dependent optical absorption

Fig. 3.14 shows the absorption spectra at room temperature of films having the same thickness (410 nm) and different compositions (e.g., 5 to 30 at.wt.% Cu and 100% GeO₂). It can be seen that the absorption edge moves towards higher wavelengths as the Cu concentration increases. Furthermore, Each spectrum can be separated into two distinct regions ; the power law region and the

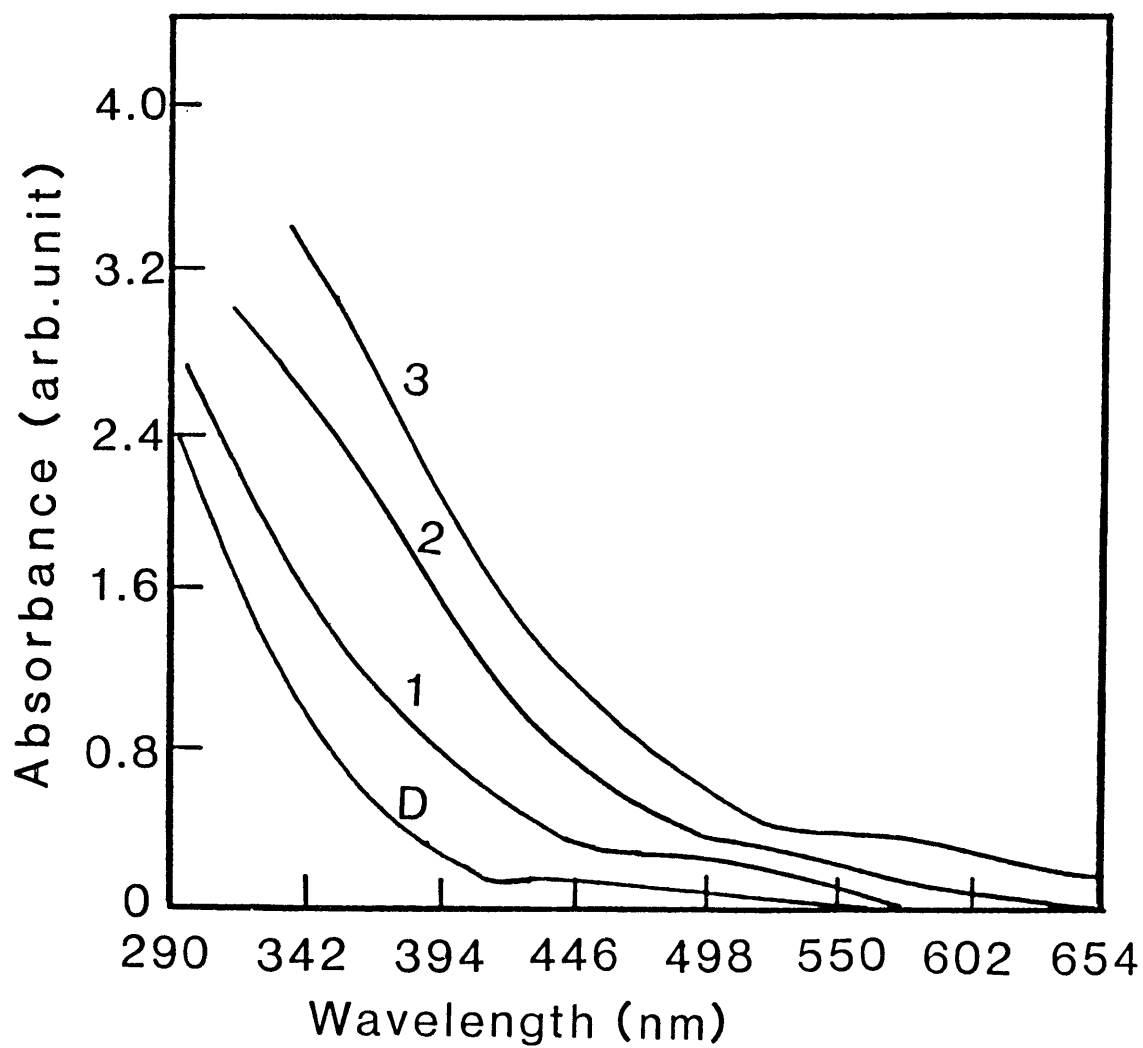


Fig.3.14 : Absorption spectra for unannealed films (410 nm) having different compositions (1) 5 at.wt.% Cu ; (2) 20 at.wt.% Cu ; (3) 30 at.wt.% Cu and (D) 100 % GeO₂

Urbach region. The power law region is again analyzed by plotting $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$), as shown in fig.3.15. For each composition, the graphs are linear in the higher absorption region ($\alpha(\nu) \geq 10^6 m^{-1}$) implying that the absorption process is dominated by allowed indirect transitions predicted by equation (3.16). The values of E_{opt} (in the range 1.99 to 2.86 eV) are obtained from the extrapolation of the linear portions and are listed in Table 3.3. It is observed that the values of E_{opt} decreases with increasing Cu concentration and are consistent with an increase in band tailing (fig.3.14).

Fig. 3.14 shows that the optical absorption edges in all cases are characterized by an exponential tail for values of the $\alpha(\nu) < 10^6 m^{-1}$. The exponential dependence of $\alpha(\nu)$ on $h\nu$ in fig. 3.16 indicates that films of varying compositions obey Urbach rule (eqn. 3.17). The values of E_e , calculated from the slopes, lie in the range 0.47 to 0.64 eV for samples 1 (5 at.wt.% Cu), 2 (20 at.wt.% Cu) and 3 (30 at.wt.% Cu). These values are listed in Table 3.3. It is observed that E_e increases with increasing copper content, which is consistent with decreasing optical gap E_{opt} .

Table 3.3 Optical energy gap (E_{opt}) and width of the tail states (E_e) of 410 nm thick unannealed samples 1, 2, 3 and D (100 % GeO_2) deposited at a substrate temperature of 303 K and a vacuum pressure of 10^{-3} Pa.

Samples	Mean deposition rate (nm/s)	E_{opt} (eV)	E_e (eV)
1	3.2	2.24	0.47
2		2.11	0.50
3		1.99	0.64
D		2.80	-

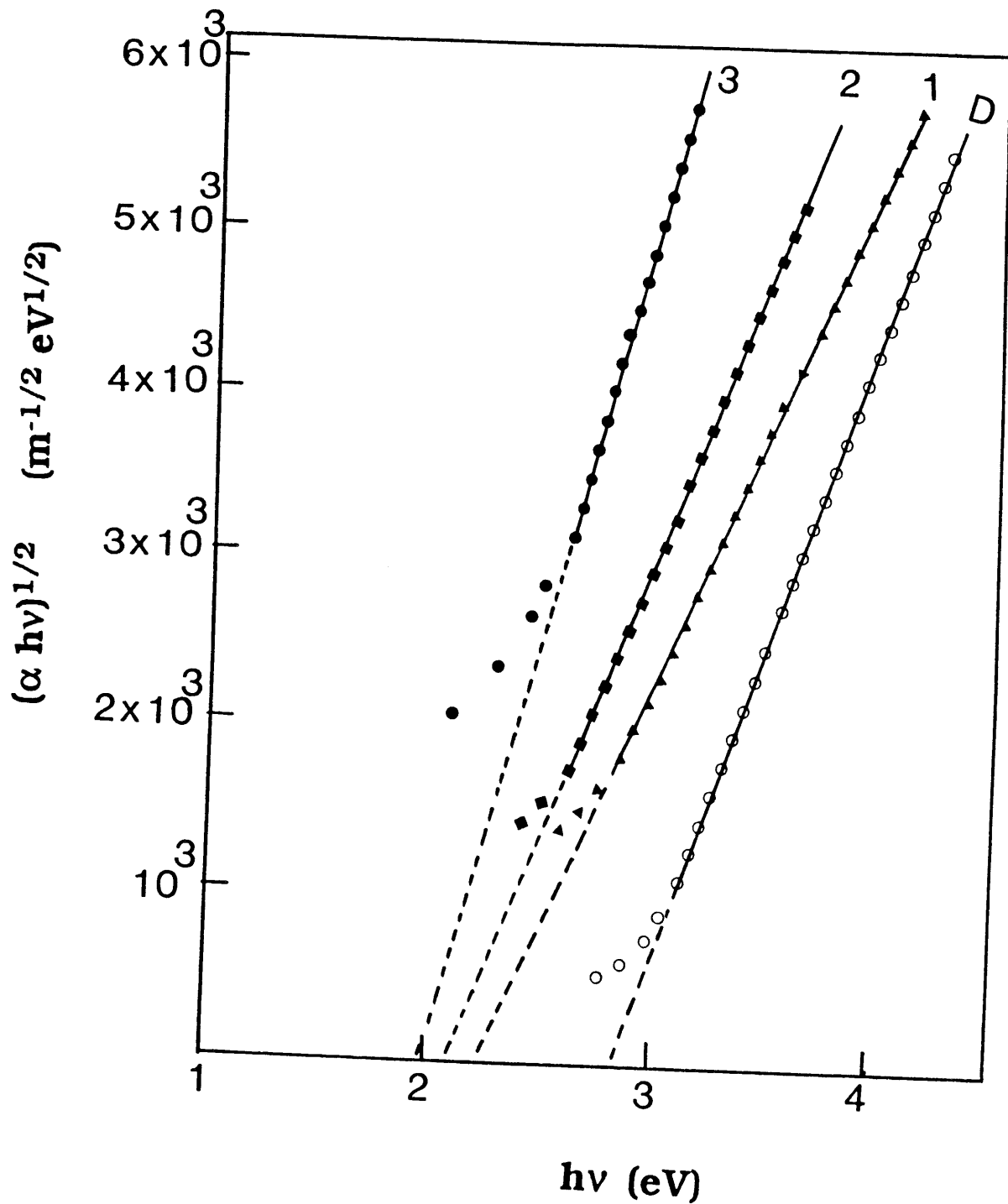


Fig.3.15 : Optical absorption spectra for samples 1, 2, 3 and D replotted in accordance with equation (3.16).
 (1) 5 at.wt.% Cu ; (2) 20 at.wt.% Cu ; (3) 30 at.wt.% Cu
 and (D) 100 % GeO₂.

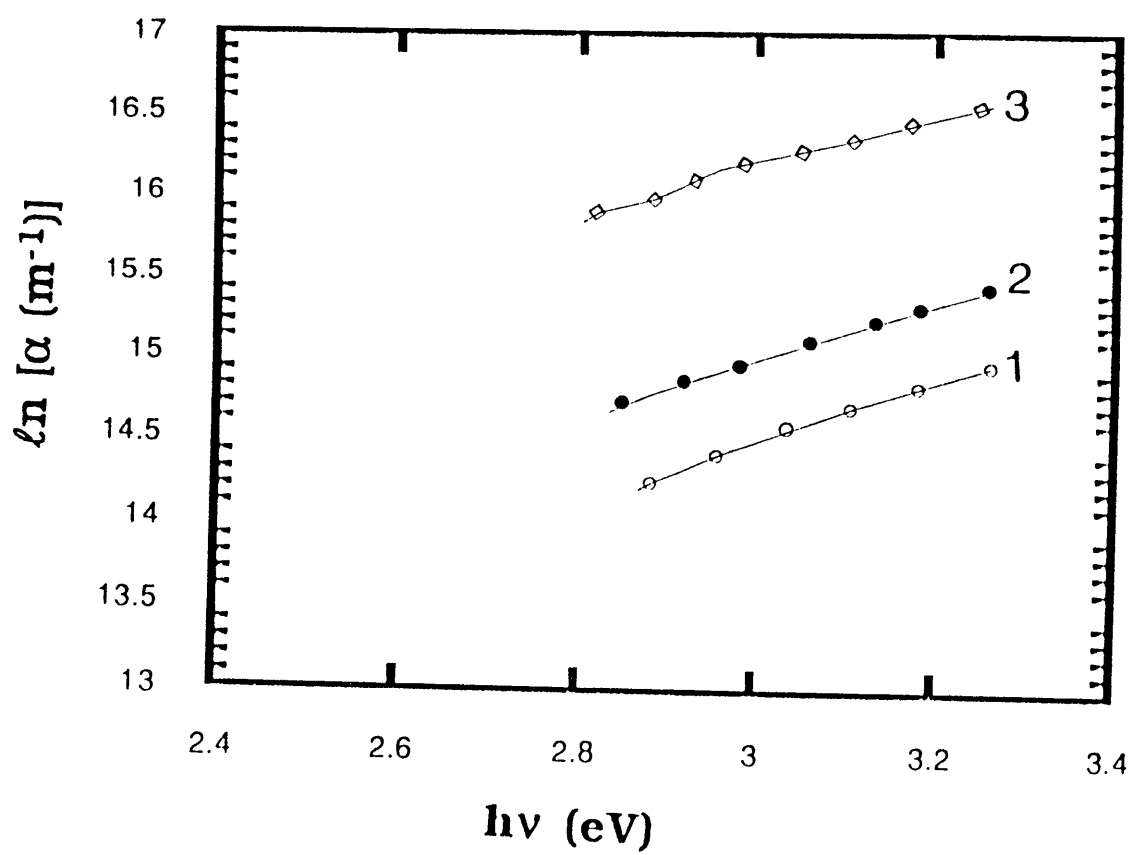


Fig.3.16 : Urbach behaviour of the absorption edge of the films (410 nm) having different compositions (1) 5 at.wt.% Cu ; (2) 20 at.wt.% Cu and (3) 30 at.wt.% Cu.

The values of E_{opt} and E_e compare favourably with those observed in Mn-SiO [Al-Ani et al. 1984] and Cu-SiO [Khan et.al. 1994]. For 300 nm thick Mn-SiO cermet, the values of E_{opt} were reported in the range 1.40 to 2.20 eV for different Mn concentrations, whereas for 300 nm thick Cu-SiO cermet system the reported values of E_{opt} vary between 1.98 to 2.71 eV for various Cu concentrations. For Mn-SiO system, the value of E_e was as high as 1.10 eV, whereas for Cu-SiO cermet the values of E_e lie in the range 0.23 to 0.72 eV.

The causes of the exponential tails have been discussed in section (3.5.2). Variation of E_e with compositions further confirms Tauc's [1966] hypothesis that carrier transitions take place between localized states in the band tails. A probable explanation of the variation of E_{opt} with compositions lie in the existence of localized states within the band gap. As mentioned in section (3.5.1), incorporation of copper into the matrix of GeO_2 introduces defect states. As copper content increases, the density of dangling bonds increases leading to increasing structural and compositional disorder. Consequently, the exponential edges broaden and shifts towards the Fermi level. This results in the reduction of E_{opt} .

It should be noted that E_{opt} obtained by the above analysis is expected to be smaller than the mobility gap ($E_C - E_V$) [Davis et al. 1970]. To take this point further, it is noted (see section (4.4.2)) that the high temperature thermal activation energy, found from $\ln \sigma$ vs $1/T$ plot, for the same samples decreases from 0.77 to 0.66 eV with increasing copper content. This observation indicates that an increase in E_e corresponds to a decrease in activation energy and consequently E_{opt} decreases. Furthermore, in each case E_{opt} is greater than twice the activation energy which suggests that,

depending on the type of charge carriers, transitions take place from the impurity band to the conduction or valence band mobility edge. This implies that E_{opt} is smaller than the mobility gap by the width E_e of the range of localized states.

3.5.4 The refractive index $n(\lambda)$ and the extinction coefficient $K(\lambda)$

The refractive index $n(\lambda)$ was calculated from the transmission spectra of sample C (see Table 2.1 and fig. 2.5) using the Swanepoel technique. The values lie in the range 2.26 to 2.39 in the wavelength range 1850-600 nm. This is a medium absorption region with $\alpha(\nu) \leq 10^6 m^{-1}$. Transmission in this region is around 80%. Fig 3. 17 shows the $n(\lambda)$ vs λ graph at room temperature (303 K). Clearly $n(\lambda)$ increases monotonically with decreasing wavelength. In the region of strong absorption i.e. $\alpha(\nu) \geq 10^6 m^{-1}$ corresponding to the wavelength range 600-270 nm, the transmission decreases rapidly and the interference fringes disappear. As a result, it is impossible to calculate $n(\lambda)$ in this region from the transmission spectrum. However, the calculated values of $n(\lambda)$ in fig. 3.17 can be fitted to a three term Cauchy dispersion relationship

$$n(\lambda) = \frac{a}{\lambda^2} + \frac{b}{\lambda} + C \quad (3.25)$$

for the extrapolation of $n(\lambda)$ to shorter wavelengths. A least-squares fit of these calculated values yield,

$$n(\lambda) = \frac{9.67 \times 10^4}{\lambda^2} - \frac{81.11}{\lambda} + 2.28 \quad (3.26)$$

with $\lambda^2 \cong 10^{-3}$. With the values of a , b and c from equation (3.26), a least-squares fit is performed to extrapolate the values of $n(\lambda)$ to shorter wavelengths. The entire $n(\lambda)$

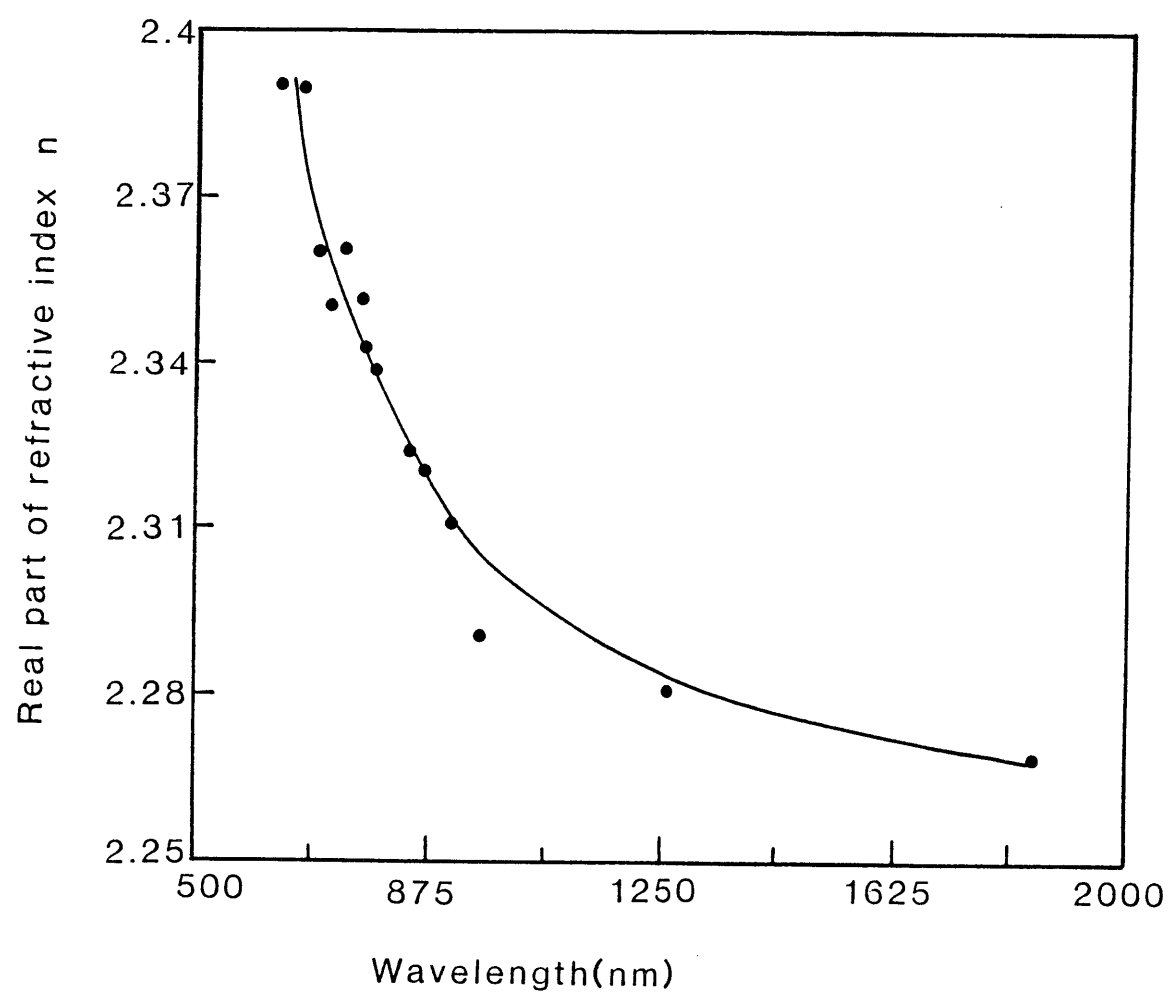


Fig.3.17: Spectral dependence of the refractive index $n(\lambda)$ on wavelength at room temperature for the sample C (e.g. 30 at.wt.% Cu)

spectrum for the medium and strong absorption regions are shown in fig. 3.18. It is seen that $n(\lambda)$ varies between 2.26 to 4.29, corresponding to the wavelength range 1850 nm to 200 nm.

It is interesting to note that the Swanepoel method has been used widely to determine the values of $n(\lambda)$, $K(\lambda)$ and thickness of the films to an accuracy of $\pm 1\%$. As a test of his model, Swanepoel [1983] obtained the values of $n(\lambda)$ for a:Si in the weak absorption region by assuming a two-term Cauchy relationship: $n(\lambda) = a/\lambda^2 + C$. A least-squares fit yielded $a = 3.02 \times 10^5 \text{ m}^2$ and $C = 2.595$. Marquez et al. [1992] calculated the values of $n(\lambda)$ in the medium-absorption-region using equation (2.11) for As_2S_3 thin films. These values were then extrapolated to shorter wavelengths to yield $a = 6.91 \times 10^4 \text{ m}^2$ and $C = 2.30$, in striking agreement with our results.

Fig. 3.19 illustrates the spectral dependence of $K(\lambda)$ on photon energy for sample C. In this figure three spectral regions can be identified. In the visible region (800 to 500 nm or 1.5 to 2.0 eV) K is very small corresponding to smaller refractive indices (2.31 to 2.50). This is a low and/or medium absorption region with transmission around 80%. At the approach of the band gap (1.99 eV) K increases rapidly in the spectral region 600 to 300 nm. This is a strong absorption region. Fig. 3.18 shows that this region also marks a sharp increase in the values of $n(\lambda)$ i.e. 2.5 to 4.5. It is believed that the identical cut-off wavelength (about 600 nm), below which both $n(\lambda)$ and $K(\lambda)$ show a remarkable increase, marks the onset of the band gap which is around 2 eV. This result is in striking agreement with the value of E_{opt} (1.99 eV) found from the x-intercept of the sample C curve (fig. 3.10). Above 3.5 eV, the film becomes transparent again. Such dispersion of $K(\lambda)$ is usually attributed to excitation of carriers from impurity band to the conduction band.

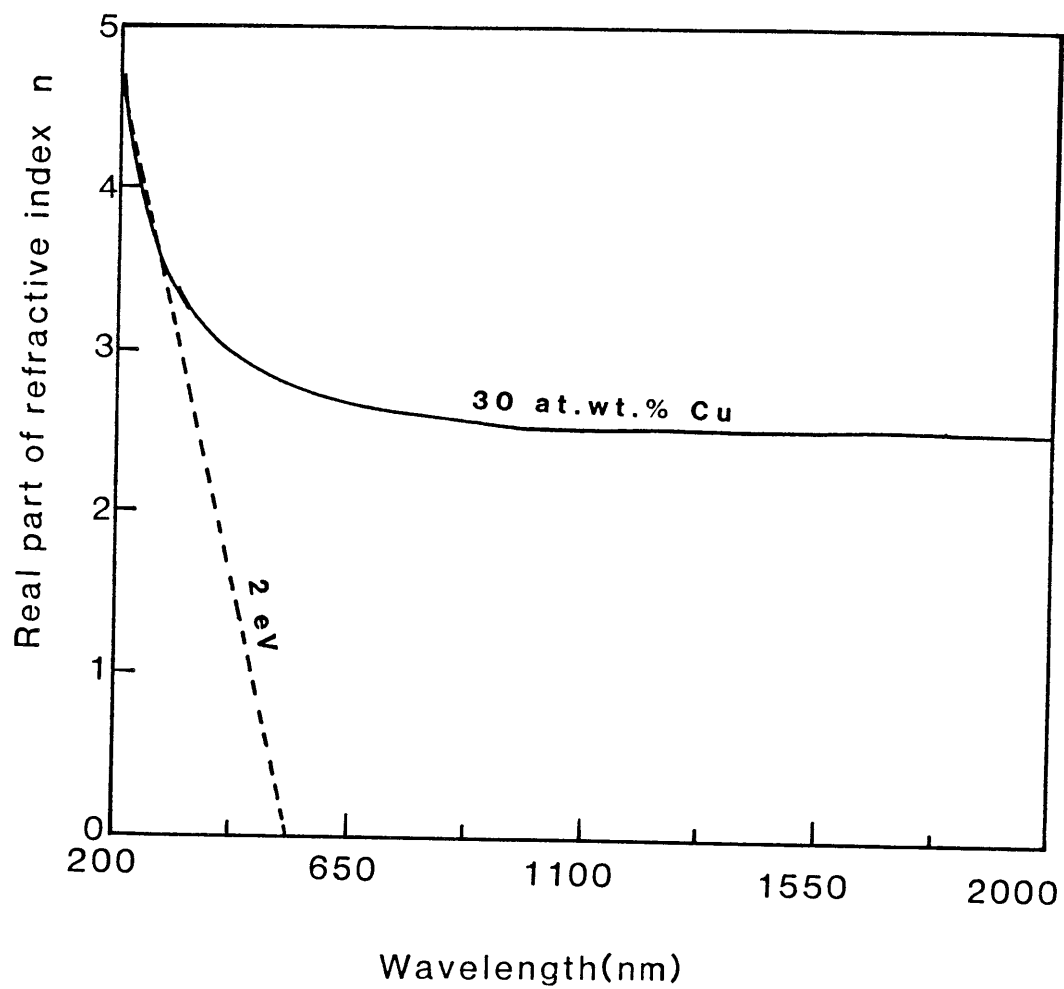


Fig. 3.18: A least-squares fit of the data of fig. 3.17 extrapolated to shorter wavelengths.

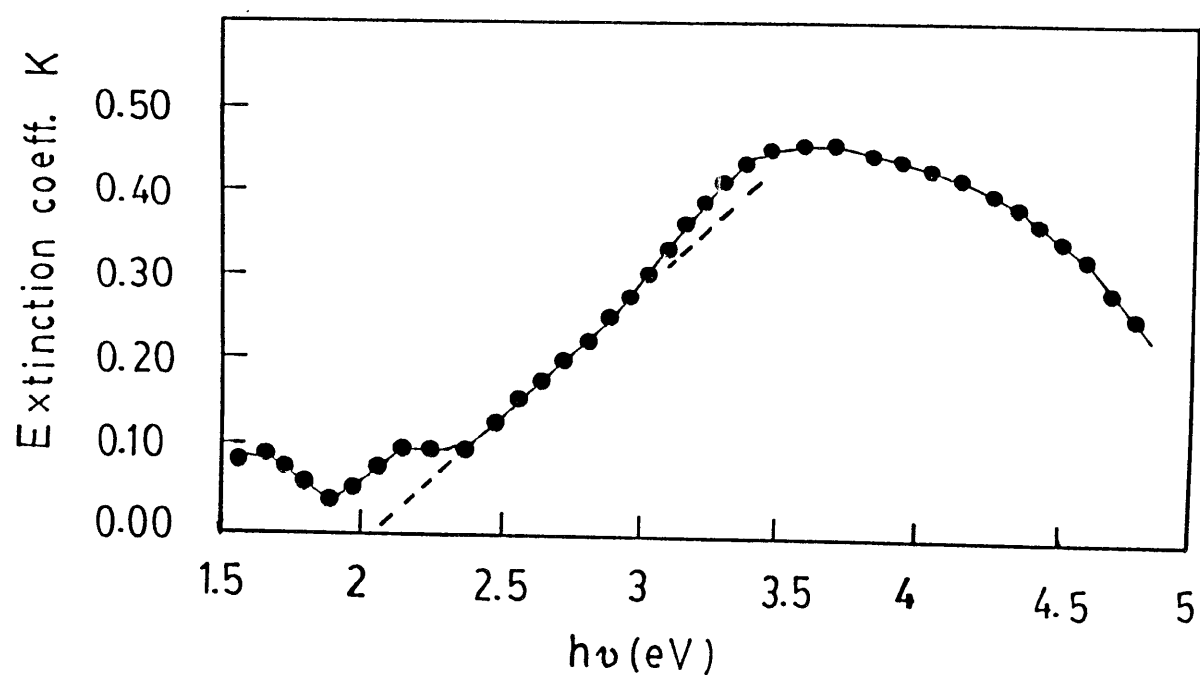


Fig.3.19 Spectral dependence of $K(\lambda)$ on photon energy for sample C .Broken line represents the onset of the optical gap (2 eV) corresponding to the cut-off $\lambda \approx 600$ nm in (fig. 3.18).

DC CONDUCTION MECHANISM

4.1 Introduction

The temperature-dependence of DC conductivity together with the studies of optical absorption, Hall effect, thermopower and AC conductivity yield valuable information about the transport mechanisms in amorphous semiconductors. At low metallic concentration (i.e. in the dielectric regime), it is widely believed that a multicomponent system, such as a granular metal or cermet film consists of metal islands dispersed in a continuous insulating matrix [Neugebauer et al. 1962, Coutts 1969, Hill and Coutts 1977, Morris 1972]. These films have a similar structure to that of a discontinuous metal film with negative temperature coefficient of resistance (TCR). Various attempts have been made to develop consistent theoretical models to account for the observed conduction mechanisms in these materials [Neugebauer et al. 1962, Coutts 1969, Abeles et al. 1975, Hill et al. 1977, Schabowska et al. 1986, Sheng 1992]; conduction may be due to either carrier transport via extended states at high temperatures or thermally-activated carrier hopping between localized sites at low or intermediate temperatures. Specific mechanisms depend on the size and spacing of the metallic grains embedded in the dielectric matrix, as well as the temperature of variation. Results of a large body of experimental investigations [Miller et al. 1970, Morris 1972, Le Comber et al. 1972, Nagels et al. 1973, Castro et al. 1980, Gladun et al. 1984, Schabowska 1985, Steele et al. 1987; 1988, Posadowski 1988, Song et al. 1989, Rahman et al. 1994] indicate that the conductivity is an exponentially-activated process. The activation energy passes through a transition point,

changing the transport mechanism from carrier hopping via localized states to conduction via extended states. The Neugebauer-Webb model [1962], which assumes uniform metal-island sizes and inter-island distances, predicts that the conductivity has an exponential dependence on reciprocal temperatures whereas the activation energy is a well defined parameter independent of temperature. However, experimental results of different metal and dielectric films suggest that the activation energy does show significant dependence on the temperature. In this case, the conductivity σ has a temperature dependence in the form of T^{-n} with n lying between 0.3 to 1, depending on the temperature of observation. This observation led Hill and Coutts [1977] and Coutts [1969] to modify the Neugebauer-Webb model in which the temperature variation of particle sizes and inter-island distances on DC conductivity were taken into account. Many features of the observed conduction mechanism are found to agree with the predictions of this model.

In several binary and multicomponent systems, common experimental features were observed [Miller et al. 1970, Nagels 1979, Steele et al. 1992, Rahman et al. 1994]. These features include strong temperature dependence of the conductivity at high temperature and weak thermal activation at lower temperature. In addition, the thermopower has a smaller temperature dependence whereas the Hall mobility has a low thermal activation which increases with increasing temperature and often exhibits a sign opposite to that of the thermopower. These observations led Nagels et al. [1973] to formulate the so-called two-channel model in which the entire conductivity curves are decomposed into two exponential functions. The first describes the conduction through localized states while the second is via the extended states. The two mechanisms observed contribute almost equally to the overall conductivity. When the rate constants of these

two exponential functions are significantly different, a kink in the conductivity curve will be observed.

While equal contributions from two competing conduction paths can sometimes account for the experimental data, a wide variety of experimental works on cermet films such as Au-SiO [Morris 1972, Miller et al. 1970, Steele et al. 1987, 1988, 1992], Al₂O₃ [Devenyi et al. 1977], Cr-SiO [Schabowska et al. 1986], and Cu-GeO₂ [Rahman et al. 1994] appears to argue against such interpretations. Alternatively, these results are compatible with small polaron hopping.

In the following sections brief descriptions of various conduction models together with some basic expressions are given. In the rest of the sections experimental results obtained on Cu-GeO₂ films and their interpretations on the basis of these conduction models are presented.

4.2 The conduction models

4.2.1 Neugebauer-Webb model

Electrical conduction in thin evaporated discontinuous films are usually explained in terms of the Neugebauer-Webb [1962] model. In this model a film is assumed to consist of small discrete metal islands dispersed in a continuous insulating matrix. These films have similar structures to those of discontinuous metal films with negative TCR. The negative TCR suggests that charge carriers, created by thermal-activation processes over the electrostatic potential barrier between two sites (islands) are either transported by thermionic emission or by tunneling from one site to the other. In both cases, the current produced due to the overlap of the potential field between two sites depends on the height

of the electrostatic potential barriers between the islands. Neugebauer and Webb contend that the tunneling current will exceed the thermionic current at any given temperature if the barrier width is small enough (i.e. < 8 nm at 300 K and < 13 nm at 200 K). The model assumes that the film consists of a regular array of uniformly distributed small metal islands of linear dimension r . These islands are separated by a small distance R through the insulating matrix (fig. 4.1). At thermal equilibrium the number of charge carriers created by the thermal energy supplied is given by

$$n = Ne^{-\frac{E_a}{kT}} \quad (4.1)$$

where N is the total number of metal particles in the film, E_a is the effective activation energy needed to transport charge from one initially neutral island to another some distance apart. Assuming a two-site interaction between electrons (or holes), the activation energy $E_a \propto e^2/Kr$, where K is the dielectric constant of the surrounding medium. The conductivity σ is calculated in the limit where $n \ll N$ and $kT \ll E_a$

$$\sigma \approx \frac{1}{r} R^2 e^2 D \exp\left(\frac{-e^2/Kr}{kT}\right) \quad (4.2)$$

where D is the transmission coefficient which depends exponentially on R . Equation (4.2) can be written in the standard form as,

$$\sigma \approx \sigma_0 e^{-E_a/kT} \quad (4.3)$$

where σ_0 is equal to $R^2 e^2 D/r$ and $E_a = e^2/Kr$. The above form of equation (4.3) predicts an ohmic behaviour at low applied electric field. The conductivity has an exponential dependence on reciprocal temperature and a marked dependence on the island size (r) and inter-island

spacing (R). In this model, r , R and D are assumed to be uniform and constant, and hence σ_o is a constant leading to a single-valued, well-defined activation energy E_a . Furthermore, the term e^2/Kr relates the linear island-dimension to the activation energy, implying that the thicker the film, the smaller will be the activation energy. The temperature coefficient of resistance (TCR) is given by,

$$\alpha = \frac{1}{R} \frac{dR}{dT} = -\frac{E_a}{kT^2} \quad (4.4)$$

where R is the resistance of the material, given by $R = R_o e^{E_a/kT}$.

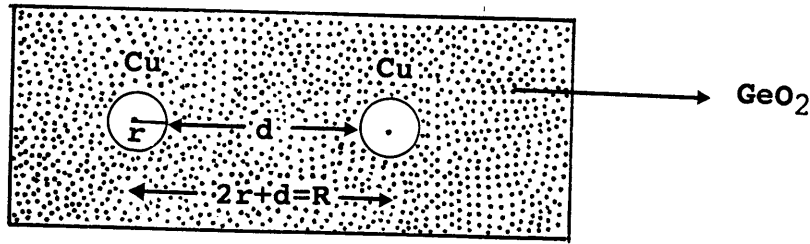


Fig.4.1: Two metal islands of linear dimension r separated by a distance $R = 2r + d$ in the GeO_2 matrix. d is the inter-island gap.

Equation (4.4) suggests that the TCR is negative for thermally-activated processes. This model was found to satisfy many features of the conduction mechanism observed in granular metal films like, Au-SiO [Morris 1972], Cr-SiO [Glang et al. 1967, Schabowska et al. 1986] and Cu- GeO_2 [Al-Saie et al. 1993]. However, the model is an idealized picture in which the temperature dependence of R and E_a were neglected, and an almost uniform size of the metal-particle was assumed. These unrealistic assumptions result in a negative TCR and a single-valued activation energy. In many experimental investigations, deviation from such a idealistic behaviour has been

reported [Coutts 1969, Gladun et al. 1985, Steele et al. 1987, 1988; Rahman et al. 1994]. For thicker films, where islands join together to produce a continuous matrix a broader distribution of particle sizes(r) may exist. In this case, a non-linear behaviour of $\ln \sigma$ vs $1/T$ giving rise to a spectrum of activation energies was observed experimentally. The dependence of r , R , and E_a on temperature also leads to the observation of both positive and negative TCR, as given by Baynes [1983], viz.

$$\alpha = \frac{4\pi}{h} (2m\phi)^{1/2} \left(\frac{d}{T} - \frac{e^2}{krKT^2} \right) \quad (4.5)$$

Here, d is the inter-island gap width, ϕ is the average height of the potential barrier between islands and $R = (2r + d)$.

Equation (4.5) explains the observation of both positive and negative TCRs in discontinuous films as being an interplay of the variation in the particle spacing (R) with T and the activation energy term. Thus, depending on the relative predominance of the two terms, a positive or a negative TCR may exist.

4.2.2 Hill-Coutts model

This formalism is an extension of the Neugebauer-Webb model in which a cermet structure is also assumed to consist of discrete metal islands dispersed in a continuous dielectric medium. While the N-W model considers a highly regular array of uniform particle sizes and spacing, the Hill-Coutts model [1977] takes a more realistic approach by examining the effects of the distribution of particle sizes and spacing on the transport properties. Consequently, the activation energy will not assume the simple nearest-neighbour coulombic

energy form (i.e. $\frac{e^2}{Kr}$); rather, a statistical approach has to be considered. In this approach the various conduction paths available to a carrier fixed on a particular island site have to be taken into account. The effective activation energy E_a will be the weighted mean of the contributions from the nearest few sites.

At very high temperatures, the irregular structure will be more uniform and ordered. In addition, particle sizes and spacing tend to be uniform, and contributions from the distant sites can be neglected. In this description, charge transport can occur between nearest special neighbours giving rise to a well-defined activation energy, as predicted by N-W model. However, at low temperatures, the model predicts, that more than one conduction path can contribute to the overall conductivity which has the form

$$\sigma \propto e^{[-(E_a/kT)^n]} \quad (4.6)$$

At high temperatures, the behaviour of the conductivity follows n equal to 1 with a single-valued well-defined activation energy. On the other hand, at lower temperatures, a variable range-type conduction will occur corresponding to n equal to 1/3. Between high and low temperatures, the model predicts that there will be a limited transition region in which the exponent n equal to 1/2 may be expected.

In contrast to the N-W model, the temperature dependence of the transport properties are found to be insensitive to the particle sizes. This effect will be averaged or eliminated by weighting the contributions from various conduction paths. The main effect of the particle size distribution is to control the temperatures at which transition between various power-law regions occur. Many features of this model have been found to be consistent

with experimental observations in flash-evaporated Cr-SiO [Schabowska et al. 1986] and in electron-beam evaporated Cu-GeO₂ films [Al-Saie et al. 1993] with the exponent n lying in the range 0.3 to 1. A behaviour corresponding to n equal to 1/2 was observed in cermets such as Au-Al₂O₃, W-Al₂O₃ [Abeles et al. 1975 a, b], Au-SiO₂ [McAlister et al. 1984, 1985] and Cr-SiO₂ [Gladun et al. 1984].

In the present work a negative TCR was observed for all the specimens. Therefore, we assume that the metal grains form isolated islands in the GeO₂ matrix, and conduction occurs between two sites due to thermal-activation. The mechanism of charge transfer may be due to tunneling, hopping, or a combination of both mechanisms [Mott et al. 1979, Sheng 1992]. In this case, the conductivity is predicted to follow

$$\sigma = \sigma_0 e^{-2\alpha R} e^{-E_a/kT} \quad (4.7)$$

α is the decay rate of the carrier wave function in the insulating matrix. For $E_a < kT$ quantum mechanical tunneling predominates and for $E_a > kT$ the hopping mechanism dominates.

The Hill-Coutts model considers two initially neutral islands in fig 4.1. The energy required to place a charge e on the first neutral island is e^2/Kr and to place a charge e on the second island is $\frac{e^2}{K(2r+d)}$. Therefore, the energy required to remove a charge from one initially neutral island to an other neutral island is given by,

$$E_a = \frac{e^2}{Kr} - \frac{e^2}{K(2r+d)} \quad (4.8)$$

or

$$E_a = \frac{e^2(r+d)}{Kr(2r+d)} \quad (4.9)$$

Equation (4.9) suggests that for $d=0$ where the islands join geometrically forming a giant metallic cluster, conduction will not be thermally-activated. In this case the DC conductivity follows a percolation power-law [Coutts 1969, Sheng 1992, Kolek 1993]. In the present study, this aspect of the conduction mechanism is not of primary interest and therefore, will not be discussed any further.

4.2.3 Band model

This model is frequently used to determine the density of states in amorphous semiconductors and is supported by a large amount of experimental measurements on chalcogenide glasses, transition metal oxides, hydrogenated amorphous silicon and cermets. This model addresses the existence of localized states in the tails of the valence and conduction bands, and of a mobility edge separating extended states from localized states. The model, which is based on Anderson's [1958] theory of localization, explains that the localized states in the gap arise from random potential-fluctuations caused by such structural defects as dangling bonds, vacancies and non-bridging atoms [Mott et al. 1975, Owen et al. 1976]. Mott [1967, 1970] and Davis et al [1970] pointed out that a mobility edge would separate energies of the extended and localized states. Several models have been proposed for the band structure of the amorphous materials, of these models the most important ones are the CFO model and the Davis-Mott model.

4.2.3.1. Cohen-Fritzsche-Ovshinsky (CFO) model

Consider the schematic density of states distribution in fig 4.2 in which $N(E)$ denotes the number of states per unit volume as a function of the electron energy E . The energy spectrum is divided according to the electronic

character of the states i.e. the extended states (ES), the localized tail states (TS) and the gap states (GS). ES lies above conduction band energy level E_C and below energy E_V in the valence band. The tail and gap states are localized in the sense that electrons in these states have wave functions which decay exponentially in phase space.

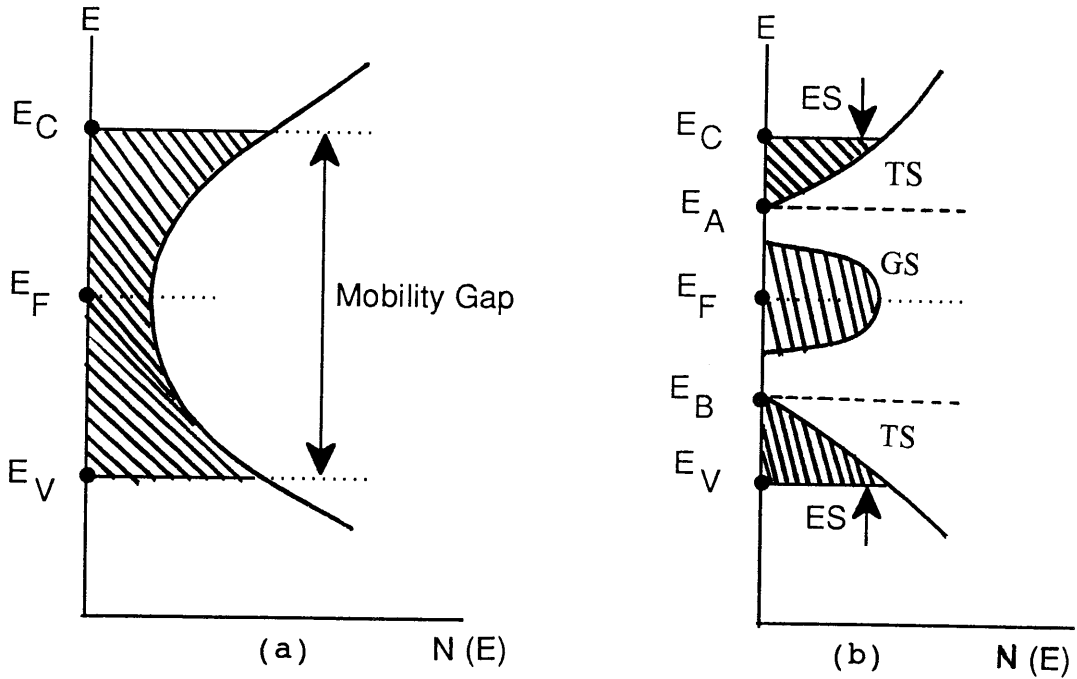


Fig.4.2: Density of states as a function of energy for amorphous semiconductors: (a) Overlapping conduction and valence band tails (CFO model) (b) The Davis-Mott model showing a band of compensated levels in the middle of the gap.

The CFO model (fig. 4.2a) assumes that the valence and conduction band-tails extend throughout the mobility gap in a featureless distribution. Overlap of these states occurs near the centre of the gap, pinning the Fermi level in the middle. Although this model was originally proposed for the multicomponent chalcogenide glasses used in switching devices, for many years this model was regarded as characteristic of amorphous materials. The model suggests that in the chalcogenide glasses

structural disorder is sufficiently great that the tails of the conduction and valence bands are broadened and deepened to the extent that they spread across the gap and overlap. This results in the destruction of the sharpness of the band edges. Although the concept of a mobility gap as predicted by this model is widely accepted, the featureless distribution of localized states throughout the gap contradicts the sharp optical absorption edge observed in most amorphous semiconductors.

4.2.3.2 Davis-Mott model

The Davis-Mott model [1970] is quite similar to the CFO model except that the localized tail-states are much narrower and extend for only a few tenths of an electron volt into the band gap. In addition to the tail-states, this model predicts a band of levels near the middle of the gap resulting from defects such as dangling bonds, vacancies etc. in the amorphous network (see Fig. 4.2b). This model has been widely used in interpreting experimental data. Drift mobility and conductivity experiments in glow-discharge-deposited silicon [Lecomber et al. 1970, 1972] reveal the presence of sharp tail of localized states near the band edges whilst photo-conductivity results show the presence of a large number of defect states near the mid-gap.

On the basis of this model, four conduction mechanisms may be expected each of which will dominate the DC conductivity over different temperature regions. At high temperatures, conduction occurs through the excitation of carriers across the mobility gap into extended states (ES) just above E_C or just below E_V . At intermediate temperatures, charge carriers are excited into the localized states of the band tails at energies close to E_A or E_B (Fig 4.2b) and conduction may occur by hopping .

The mobility and the density of states near E_A or E_B are much lower than in the extended states. At low temperatures, conduction can occur by thermally-assisted tunneling between states at the Fermi level. As the temperature is lowered further, carriers tend to hop larger distances beyond their nearest neighbouring sites in order to find sites that are closer energetically. This is the so-called Mott-type variable-range hopping mechanism. It would appear that in order to understand and develop accurate band structure for amorphous semiconductors, contributions from all these four mechanisms must be examined.

4.2.3.2.1 Extended state conduction

In this model, conduction is due to carrier excitation across the mobility gap into the extended states above E_C or below E_V . In this case, assuming the carriers to be electrons, the DC conductivity is given by,

$$\sigma_2 = eN(E_C)kT\mu_c \exp[-(E_C - E_F)/kT] \quad (4.10)$$

where $N(E_C)$ is the density of states at E_C and μ_c is the average drift mobility or conductivity mobility of the carriers. Cohen [1970] suggested that carrier transport in this case is essentially a diffusive Brownian-type motion and therefore, the carrier mobility can be written as,

$$\mu_c = 1/6(ea^2/kT)v_{el} \quad (4.11)$$

Here a is the inter atomic separation and v_{el} is the electronic frequency $\approx 10^{15} \text{sec}^{-1}$. Using equation (4.11), the drift mobility in the extended states is estimated to be around $10 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature. From equations (4.11) and (4.10), the expression for the conductivity becomes,

$$\sigma_2 = \sigma_{02} e^{-(E_c - E_F)/kT} \quad (4.12)$$

where,

$$\sigma_{02} = \frac{e^2 N(E_c)}{6} a^2 v_{el} \quad (4.13)$$

The constant σ_{02} is generally interpreted as the minimum metallic conductivity. This is the lowest value of the electrical conductivity before the beginning of an activation process. In the case of chalcogenide and many transition metal oxide glasses σ_{02} is usually $\approx 10^2$ to $10^3 \Omega^{-1} \text{cm}^{-1}$.

4.2.3.2.2 Conduction in localized states near band tails

In localized states at energies close to E_A or E_B where $\sigma(E)=0$, conduction can only occur by thermally-activated hopping processes; the conductivity depends on the energy distribution of the density of states. Assuming conduction by electrons alone, the hopping conductivity σ_1 is given by,

$$\sigma_1 = \sigma_{01} e^{[-(E_A - E_F + W)/kT]} \quad (4.14)$$

where

$$\sigma_{01} = 1/6 [v_{ph} e^2 R^2 N(E_c)] \quad (4.15)$$

Here v_{ph} is the phonon frequency, R the hopping distance between two sites, W the hopping activation energy and $N(E_c)$ is the density of states at E_c . The mobility in this case is characterized by thermal-activation and is given by,

$$\mu_1 = \mu_{01} e^{-W/kT} \quad (4.16)$$

For a typical phonon frequency $\approx v_{ph} = 10^{13} \text{s}^{-1}$, $W=kT$, and assuming that the hopping conductivity is very close to E_c or E_v (where $R \approx a$, the average inter atomic distance), equation (4.16) yields a mobility $\approx 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Thus, near E_c or E_v , the mobility drops two orders of

magnitude when making transition from extended states to localized states. This behaviour defines the so-called mobility gap [Cohen et al. 1969, Mott 1969] which explains why many amorphous materials show a linear $\log \sigma$ vs $1/T$ plot over a wide range of temperature.

4.2.3.2.3 Conduction in localized states close to Fermi level

At low temperatures, conduction can occur by phonon-assisted hopping between localized states at the Fermi level. The mobility $\mu(E)$ for this process is given by Mott [1969] as

$$\mu(E) = [eR^2 / kT] v_{ph} e^{-2\alpha R} e^{-W/kT} \quad (4.17)$$

where the hopping distance R depends on the density of states distribution, and, therefore, is a function of energy. The term $e^{-2\alpha R}$ rises from the overlap of the wave functions on neighbouring hopping sites, α is the rate of decay of localized wave function. The term $v_{ph} e^{-W/kT}$ represents the probability that a localized carrier will hop to a new site at an energy W above the initial one. Equation (4.17), similar to equation (4.16), predicts a hopping mobility $\approx 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. In this model, the conductivity is given by Mott [1969] as

$$\sigma = e^2 R^2 / 6 [v_{ph} R^2 N(E_F) e^{-2\alpha R} e^{-W/kT}] \quad (4.18)$$

4.2.3.2.4 Variable range hopping

At very low temperatures, it is possible that phonon-assisted hopping will diminish as phonons become less energetic. In such a situation, it is possible to become energetically more favourable for a carrier to hop to larger distances in order to find sites close in energy to its initial sites. Mott's [1969] treatment of this so-

called variable range hopping process leads to a temperature-dependent conductivity of the form,

$$\sigma = (1/6)e^2 R^2 N(E_F) e^{-A/T^{1/4}} \quad (4.19)$$

or

$$\sigma = \sigma_o(T) e^{-A/T^{1/4}} \quad (4.20)$$

where

$$A = 2.1 [\alpha^3 / kN(E_F)]^{1/4} \quad (4.21)$$

and

$$\sigma_o(T) = (1/6)e^2 R^2 \nu_{ph} N(E_F) \quad (4.22)$$

Fig.4.3 summarizes the information on the electronic transport for all the conduction mechanisms. The results of extensive experimental works on amorphous materials during the past two decades appear to be in reasonable agreement with the conduction models outlined above. Some excellent reviews on this subject can be found in Nagels [1979] and Owen et al. [1976].

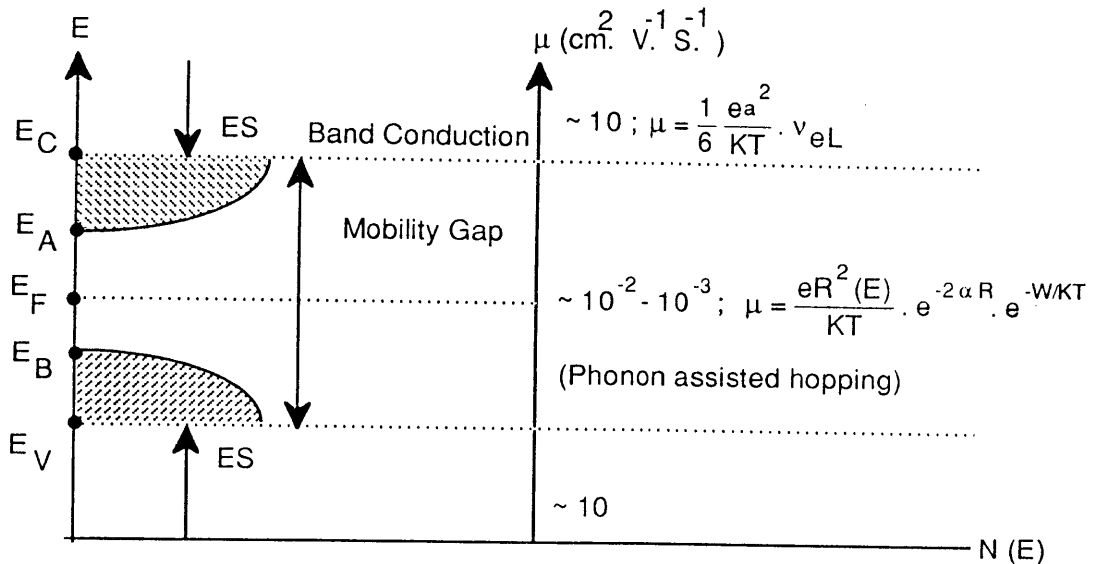


Fig.4.3 Summary of the conduction processes described in sections (4.2.3.2.1), (4.2.3.2.2) and (4.2.3.2.3). The shaded part denotes the region of localised states.

4.2.4 Two Channel model

Over a wide temperature range, the experimental measurements of DC conductivities of chalcogenide glasses [Nagels et al. 1973, Seager et al. 1973, 1975, Mott et al. 1975], amorphous silicon [Le Comber et al. 1972, 1977] and of thin cermet films [Gladun et al. 1985, Schabowska et al. 1986, Steele et al. 1987, 1988, Rahman et al. 1994] suggest that it is an exponentially-activated process. The activation energy and the pre-exponential factor in equation (4.14) will pass through a critical point changing the transport mechanism from hopping to band conduction. Furthermore, the thermopower (t_p) is found to have a smaller temperature dependence as compared to the DC conductivity with $E_a(dc) - E_a(t_p)$ being $0.1 - 0.2 eV$. The Hall mobility has an activation energy in the range $0.03 - 0.05$ eV. In addition, the Hall mobility is usually low ($10^{-6} - 10 cm^2 V^{-1} s^{-1}$), and often increases with increasing temperature, frequently exhibiting a sign opposite to that of the thermopower.

Two models are usually invoked to explain these observations : the two channel model and the small polaron model. The two channel model [Nagels et al. 1973] assumes nearly equal contributions from two competing mechanisms in which transport can occur almost simultaneously in extended and localized states. This model predicts that the two paths will contribute almost equally to the overall conductivity σ given by

$$\sigma = \sigma_2 + \sigma_1 \quad (4.23)$$

where σ_2 and σ_1 are determined from equations (4.12) and (4.14), respectively. If the rate constants of σ_2 and σ_1 differ significantly, a kink in the conductivity curve will be observed (Fig. 4.4). When the transition from one conduction mechanism to the other is gradual with almost

equal rate constants, the curve will change its slope gradually and will not differ appreciably from a straight line [Nagels 1979]. This behaviour is shown by the dotted line in fig 4.4.

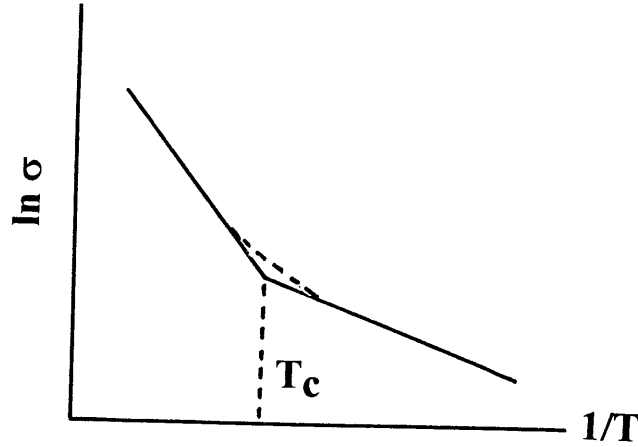


Fig.4.4 Schematic plot of $\ln \sigma$ vs $1/T$ in the range of two-path conduction. The solid line shows a kink (at T_c) indicating a sudden transition in conduction mechanism. The dotted line shows a gradual change in the conduction mechanism.

Another prediction of the model is that the thermopower is also the weighted sum of the two contributions and its behaviour around the critical temperature T_c will depend on the sharpness of the transition in DC conductivity curves.

The temperature dependence of the Hall mobility according to this model increases with increasing temperature to a constant value. The Hall mobility is given by the weighted sum [Nagels 1973, 1979],

$$\mu_H = \frac{\mu_{H2}\sigma_2 + \mu_{H1}\sigma_1}{\sigma_2 + \sigma_1} \quad (4.24)$$

where μ_{H2} and μ_{H1} are the Hall mobilities in the extended and localised states, respectively.

In the above expression, the authors assume that μ_{HI} of the localized states may be neglected, so that,

$$\mu_H = \mu_{H2} \sigma_2 / \sigma \quad (4.25)$$

Another prediction of the model is the sign anomaly in the Hall mobility. This can be explained on the basis of nearly equal mobilities of electrons and holes and nearly equal electron-hole contributions to the overall conductivity. Since the two paths contribute equally, one obtains a low Hall mobility with p-type thermopower and a negative sign; The μ_H results from the cancellation between two relatively large mobilities of opposite sign.

However, one cannot always envision a material possessing n and p type regions in reasonable proportions so as to make the Hall mobility μ_H low and to account for the sign anomaly. These restrictions impose severe limitations on this model. An alternative model due to Emin et al. [1972] and Emin [1973] is the small polaron model, in which trap-modulated hopping of carriers near the mobility edges are considered. This is discussed in the next section.

4.2.5 Small polaron model

In contrast to the CFO and Davis-Mott band models, a different approach to the understanding of the electrical transport properties of amorphous semiconductors was suggested by Seager et al. [1972] and Emin [1973]. These authors proposed that if the lattice deformation in non-crystalline materials is strong enough, this may cause small polaron formation. The presence of disorder in a non-crystalline material tends to slow down a carrier. As a result, the carrier would have a tendency to remain in the vicinity of a particular site long enough for displacement or polarization of the surrounding atoms to

take place. In its bound state with the polarization cloud, a potential well is created which leads to the trapping of the carrier. The trapped carrier and the surrounding polarized region is treated as a unit known as a polaron. In its bound state, the carrier can not move unless the polarization cloud moves with it. Consequently, a polaron possesses lower energy than a free carrier but has a larger effective mass. The decrease in energy relative to that of an electron in an undistorted lattice is called the polaron binding energy W_b .

In general, a small polaron can move by two different mechanisms. At low temperatures, polarons can move without interacting with phonons. This results in band conduction. At higher temperatures, the small polarons migrate by hopping between equivalent sites. Furthermore, an equivalent site is created by phonon-induced lattice deformation and hence, hopping can be regarded as a phonon-assisted tunneling process. Thus, polaron hopping depends on the occurrence of momentary structural fluctuations causing adjacent occupied and unoccupied sites to have coincident deformations [Holstein 1959]. At each coincident event, the carrier will have a certain jump probability, P , given by [Holstein 1959],

$$P = P_1 P_2 \quad (4.26)$$

where P_1 is the probability for the occurrence of a coincident event and P_2 is the probability that a charge will migrate during that event. The probability P_1 for coincident events with equal potential can be written as [Nagels 1979],

$$P_1 = \frac{\omega_o}{2\pi} e^{-W/kT} \quad (4.27)$$

where $\frac{\omega_o}{2\pi}$ is the phonon frequency, W is the polaron hopping energy and is related to W_b by $W = W_b/2$. The total probability p then becomes,

$$p = \frac{\omega_o}{2\pi} e^{-W/kT} P_2 \quad (4.28)$$

Two cases are generally considered :

1. The adiabatic regime in which the carrier jumps several times between coincident sites, leading to high migration probability i.e. $P_2=1$.
2. The non-adiabatic regime, in which the carrier can not follow the lattice vibrations, and the time required for the carrier to hop is long compared to the duration of a coincident event. In this case, many coincident events take place before the carrier can hop. Therefore, the probability for carrier transfer between sites becomes much smaller than unity i.e. $P_2 \ll 1$. According to Holstein [1959], P_2 in this regime is given by,

$$P_2 = \frac{2\pi}{\hbar\omega_o} \left(\frac{\pi}{WkT} \right)^{1/2} J^2 \quad (4.29)$$

Here J is the electronic overlap integral between the sites. The conductivity σ is then given by,

$$\sigma = \frac{ne^2}{kT} a^2 P_1 P_2 \quad (4.30)$$

where P_1 and P_2 are given by the equations (4.27) and (4.29) respectively and n is the charge carrier density. The conductivity mobility is given by,

$$\mu_c = \frac{ea^2}{kT} P_1 P_2 = \frac{ea^2}{kT} \frac{1}{\hbar} \left(\frac{\pi}{WkT} \right)^{1/2} J^2 e^{-W/kT} \quad (4.31)$$

Equation (4.31) suggests that the conductivity mobility is thermally-activated and increases exponentially over a broad temperature range defined by $T \geq W/k$. For $T \leq W/k$, the pre-exponential term varies as $T^{-3/2}$ and becomes dominant. Therefore, at a certain temperature the conductivity mobility is predicted to show a maximum. This behaviour totally contradicts the $1/T$ law predicted by the Davis-Mott band model (eqn. 4.11). The essential features of the polaron model summarized above will be discussed again in Chapter 5 in connection with Hall effect and magnetoresistance studies. Equation (4.31) will be used together with the expression for the Hall mobility to derive an expression for the Hall coefficient R_H .

4.3 Experimental Procedures

4.3.1 Film Preparation

Thin films of varying thicknesses (227 to 407 nm) and compositions (5, 20 and 30 at.wt.% Cu) were prepared by electron-beam evaporation of appropriate mixes of Cu (99% Adrich Chemical Co) and GeO_2 (99% Fluka A.G.) powders pressed in the shape of tiny discs at 8 tons of pressure for four minutes under vacuum. Prior to the deposition, the substrates, Corning 7059 glass slides, were cleaned and dried in a series of conventional steps and later by a glow-discharge cleaning process in vacuum. The position of the substrate, properly masked, was kept in the centre relative to the source while the films were deposited onto the substrate from a single graphite boat at a residual pressure of 10^{-4} Pa and substrate temperature of 300 K. The mean rate of deposition was 3 nm/s corresponding to the beam-voltage of 3000 V and beam-current 12-16 mA. Film thickness and deposition rate were

monitored in-situ with the help of FTM5 quartz crystal monitor(see section (2.5.2)), and were later confirmed by the method of transmission interference fringes (see section (2.5.3)).

4.3.2 DC conductivity measurements: The two probe method

For the conductivity measurements, rectangular shaped (4.5 mm x 2.5 mm) aluminum electrodes (of thickness 80 nm) were evaporated on the films in a coplanar geometry. The gap(d) between the electrodes was 1.5 mm. The main advantage of using the coplanar geometry is that the large sheet resistance of the samples generally masks any contact effects. The bias voltage applied across the gap was kept low ≈ 10 V in order to prevent resistive heating of the samples. When performing electrical measurements on high impedance cermets, spurious results can arise from a number of sources, such as resistive heating, contact resistance, leakage paths, thermal e.m.fs and external electrostatic interferences. To minimize these effects, the measuring system needs to be carefully guarded and shielded. These problems and the precaution taken against them are discussed in section (4.3.3). If contacts to the electrodes are poor, the electric field distribution in the gap will not be uniform and the equipotential lines will be distorted especially at the edges. In order to minimize this effect, the gap between the electrodes was kept as narrow as possible and two fine coated copper wires were pressed to the electrodes by high purity silver epoxy. These steps effectively reduced the current noise in the contacts. The sample was then mounted onto a specially designed Hewlett-Packard sample holder. Measurements of the I-V characteristics were completed using a constant current source (Keithely 220) and high impedance electrometer (Keithely 617) which showed that good ohmic contacts were established. The DC conductivity measurements were carried out in the

temperature range 573-323 K using a HP 4140 B PA meter which acted as a voltage source and a picoammeter. A HP 3497 A Data-acquisition unit was used to measure the potential-drop across the thermocouple. The measurement system is shown in plate 3. The samples were heated inside a Gallenkamp furnace. All measurements were carried out under the control of a HP 9145 computer. The equipment layout is shown schematically in fig. 4.5.

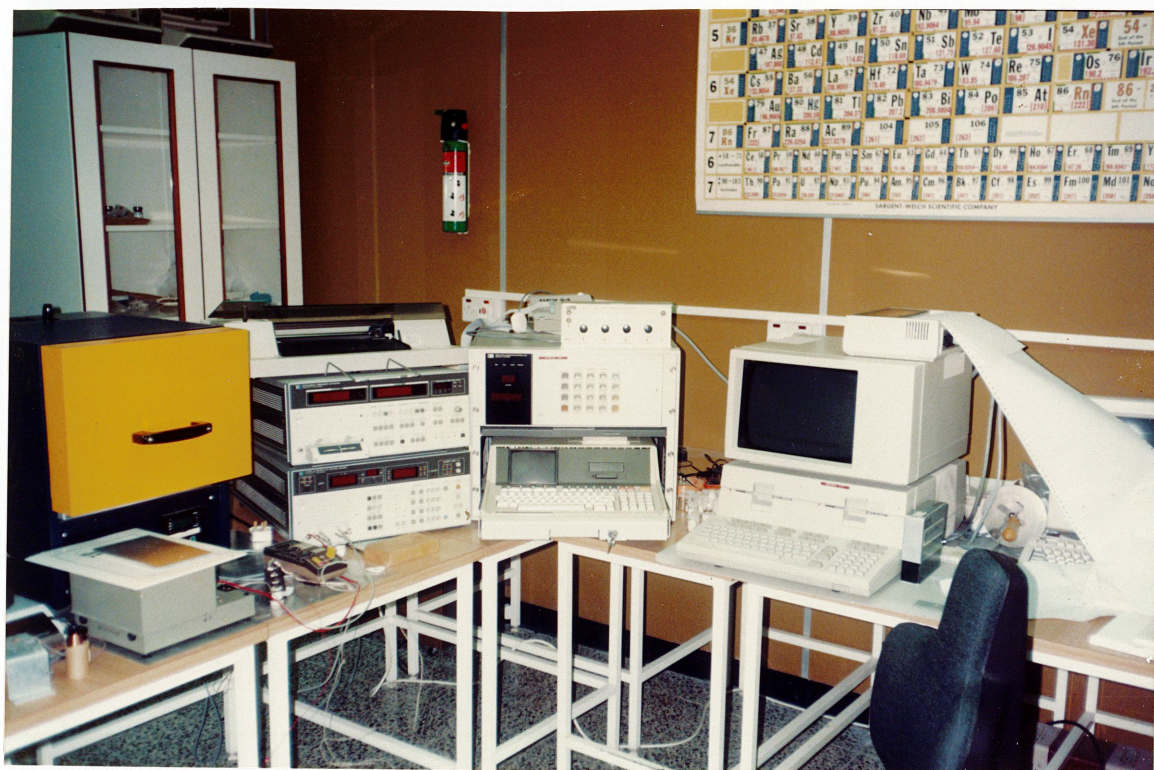


Plate 3 : Two probe DC conductivity measurement system.

4.3.2.1 HP 4140 B PA meter/DC voltage source

This equipment comprises a high stability PA meter with 10-15 A(max) resolution coupled with two programmable DC voltage sources to ensure usability in many application areas. The PA meter has a basic accuracy of 0.5% over wide measurement ranges (10^{-12} A to 10^{-2} A). The DC voltage source has an output range of ± 100 V in 100 mV steps or ± 10 V in 10 mV steps. One of the voltage sources

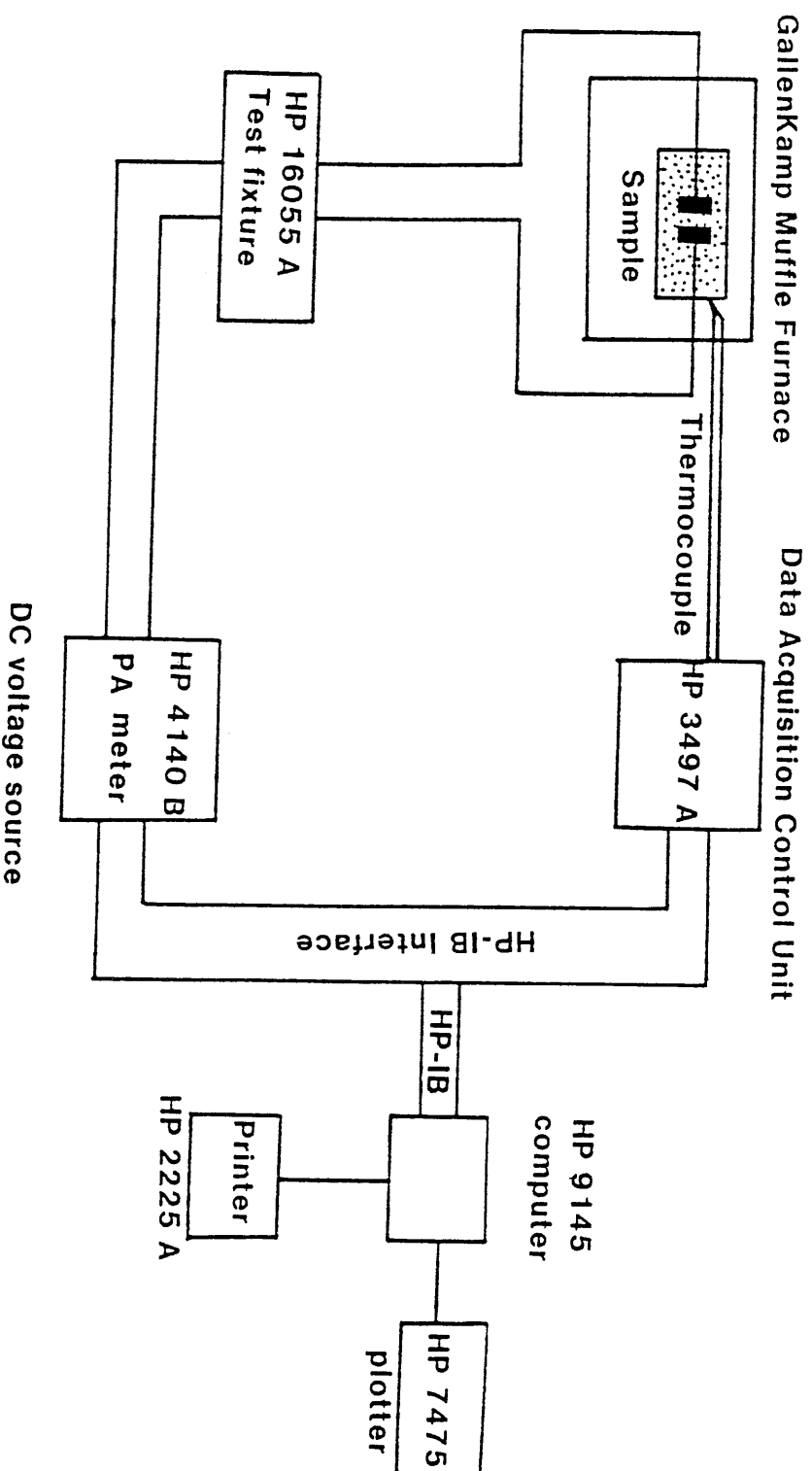


Fig.4.5 Block diagram for two probe DC conductivity measurement system.

can operate not only as a programmable DC voltage source, but also as unique stair case and ramp generator. The zero offset current capability cancels the leakage current of test leads and fixtures, and its zero offset capacitance capability cancels stray capacitance of test leads and fixtures for accurate current or capacitance measurements. The meter also provides HP-IB interface for remote control and data output via the HP-IB. Once the system was programmed, it was left overnight for data acquisition. Night was chosen so as to avoid vibration interferences to which most high impedance materials are sensitive.

To achieve stable low-current measurements at 10^{-9} A, care was taken to minimize the effects of leakage currents. This was done by employing a guard-ring where the HIGH terminal of the PA meter is guarded by the LOW terminal. The effects of externally generated noise and electromagnetic interferences were reduced by taking all measurements inside the electrostatic/light shielded Gallen Kamp Muffle furnace.

4.3.2.2 HP 3497 A : Data acquisition and Control system

This unit combines precision measurement capability with control functions. It provides precision measurements of the thermocouple and other transducers with HP-IB interfacing and control with the desk-top computer. Data inputs, such as temperature and the resistance of the samples are measured from a user-system via a thermocouple. The thermocouple converts these parameters into electrical signals which can be measured by the HP 3497 A system. The controller (desk-top computer) sends commands to the HP 3497 A via the HP-IB interface to initiate measurements and to transfer data for processing.

4.3.3 The 4-probe van der Pauw method

Of the various four-probe techniques available, the van der Pauw method [van der Pauw 1958] is the most suitable one for thin films, since the requirements of peripheral contacts to the sample permits the use of film electrodes. As mentioned earlier (see section (4.3.2)), when making conductivity and Hall effect measurements on high-resistivity materials, spurious signals can arise from a number of sources. All these factors contribute a high background voltage compared to the small voltage to be measured usually $\approx \mu V$. To eliminate these effects, the system must be carefully guarded and shielded. Common sources of errors encountered in the two probe method are the contact area-dimension, improper positioning of the contacts, irregular spacing between the contacts and contact resistances. An advantage of the van der Pauw technique is that the method requires only 4-point contact located anywhere on the periphery of a uniformly thick sample of arbitrary shape.

The apparatus which permits simultaneous conductivity and Hall effect measurements on high impedance-low mobility materials is schematically shown in fig 4.6. It typically includes a Keithley 220 constant current source, one 617 and one 614 electrometer as unity gain buffers and a model 195 A digital multimeter. The 614 electrometer was used with a model 6167 guarded-input adapter. The 617 electrometer has a built-in guard switch and, therefore, does not need external guarding. The guard ring virtually eliminates both leakage currents and line capacitance. As seen in fig 4.6, a guard ring is available for two terminals of the sample marked 3 and 4. The Terminal 2 was at circuit 'low' or ground potential, and hence, did not need any guarding. Terminal 1 was unguarded but was isolated through common grounding with electrometers. The entire system including connecting leads and

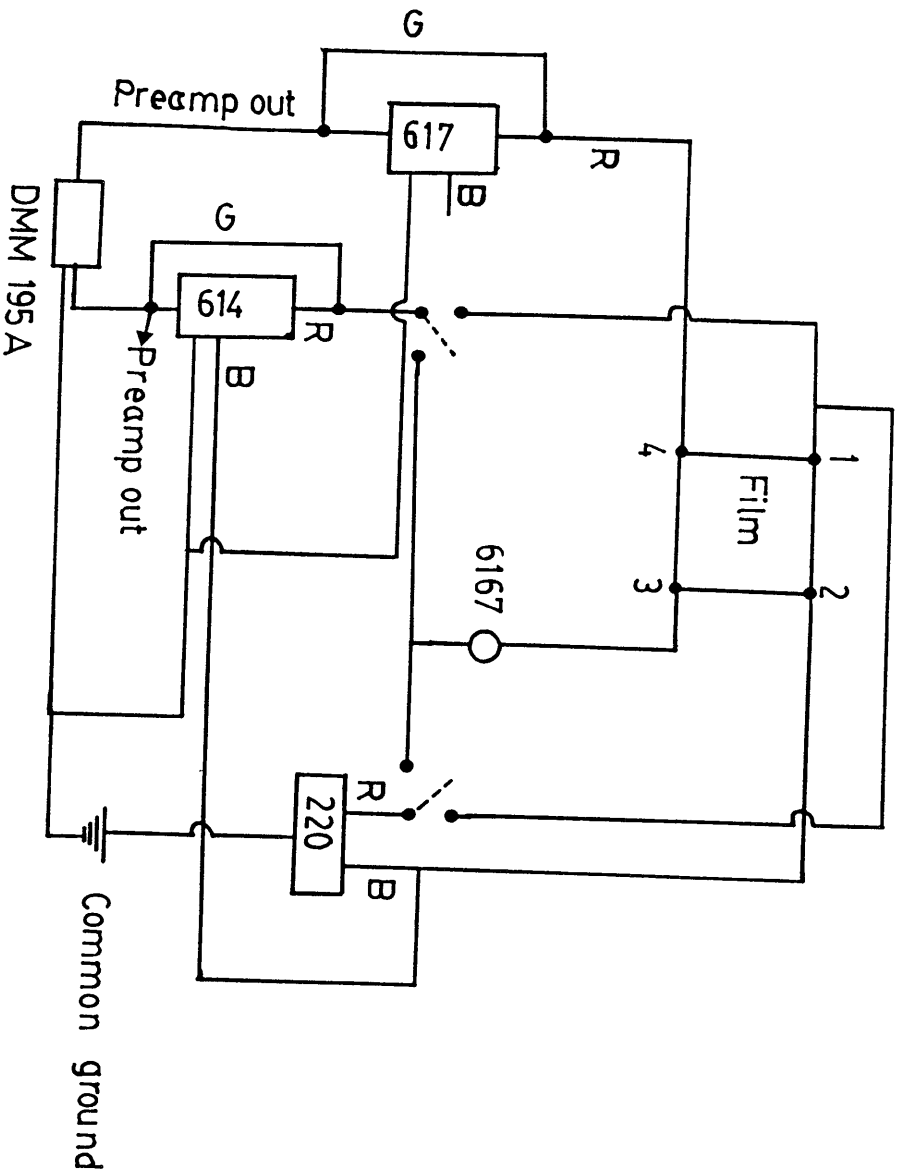


Fig.4.6: Equipment configuration for van der Pauw conductivity and Hall effect measurements. The magnetic field and switching arrangements for Hall effect measurements are not shown for the sake of space and clarity.

switching devices were housed in a Faraday-style aluminum cage to avoid electrostatic pickup.

Aluminium contacts (1 mm in diameter, 80 nm thick) were thermally evaporated onto the four corners of 4 mm x 4 mm square shaped specimens. Four fine coated copper wires were then pressed into the contacts using silver epoxy. The specimen was next mounted in a sample holder fitted with a heater and steel electrodes. A zinc-oxide filled silicone compound with high thermal conductivity (17×10^{-4} cal/cm s°C) was used to make thermal contact and to provide excellent heat transfer between the substrate and the heater. A NiCr-NiAl thermocouple was glued to the substrate with the same silicone compound and the temperature was monitored with the help of Keithley 871 digital thermometer. Proper guarding and shielding were maintained to eliminate leakage currents and line capacitance. However, resistive heating and thermal e.m.f due to temperature gradients in the contacts and connecting leads, could still persist. A low current (10^{-9} A) was used and the DMM was continually zeroed between each reading to eliminate the effects of resistive heating. To overcome the effects of thermal e.m.fs and offset voltage drift with temperature, a cycle of offset voltage was run as a function of temperature with current $I=0$. Fig 4.7 shows this variation. Background voltages were then normalized in terms of this curve and subtracted at each temperature from the DMM readings.

The DC conductivity was investigated on 410 nm thick Cu-GeO₂ films containing 5, 20 and 30 at.wt.% Cu in the temperature range 307 to 425 K. The sample holder used for the conductivity measurements did not permit measurements beyond 450 K.

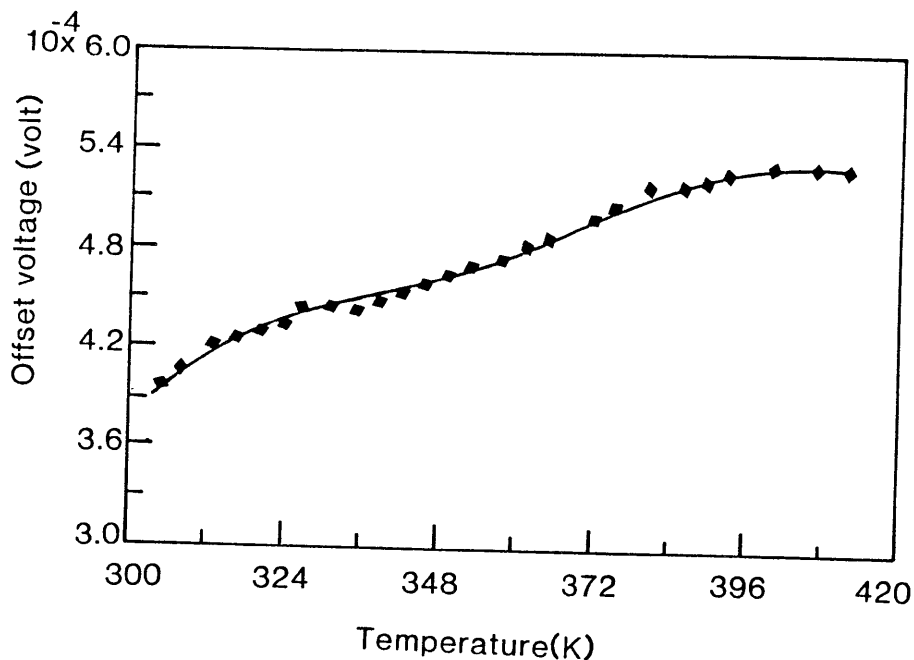


Fig.4.7: Offset voltage drift as a function of temperature.

4.3.3.1 Sources of errors and precautions taken to minimize them

Spurious effects often encountered in high impedance-low current measurements are likely to contribute background voltages which are high compared to the small actual voltage measured across the contacts. Therefore, it is imperative that these parasitic effects be minimized or eliminated through careful experimental techniques. The following list some of the sources of errors and the precautions used with each:

Error: Uncertainty or error in thickness measurements effect the calculated values of resistivity and conductivity.

Precautions: Two methods(see sections (2.5.2) and (2.5.3)) were mainly employed to improve the accuracy in thickness measurements. An average of the two measurements was used in all calculations to obtain best results.

Error: High contact resistance may lead to current noise, capacitive effects and other spurious results.

Precautions: Minimized by evaporating very small contacts and using very low-resistance, high-conducting silver epoxy for electrical contacts.

Error: Leakage paths are a major source of errors in high resistivity samples. Surface and other possible leakages in switches, wires, cables etc. may shunt some of the current around the sample. Furthermore, high values of the lead capacitance increases the time constant of the circuit.

Precautions: Minimized by introducing a guard ring and by using shielded short cables.

Error: Resistive heating due to the passage of the current through the sample. This contributes to the background voltage.

Precautions: Minimized by using a very small current 10^{-9} A and by zeroing the DMM between every reading.

Error: Thermal e.m.f.s are the most common sources of errors in low-current measurements. These arise from the temperature gradients in the sample caused by junction effects of dissimilar materials joined together.

Precautions: Minimized by using a low current; by using connecting leads of the same materials; by placing all junctions in close proximity to one another, and using the offset-compensated normalization method.

Environmental factor: A good and stable environment is crucial to making low-level measurements. Factors like temperature, humidity and electrostatic interference may effect low-level measurements. Temperature variations can cause thermal expansion or contraction of contacts in the junctions and the material itself producing noise currents. It can also increase the leakage current.

Precautions: To minimize these effects, the entire system was allowed to stabilize thermally before recording the readings. Care was also taken to keep the apparatus away from sources of mechanical and electrical vibrations and by performing the experiment in a humidity-free atmosphere.

4.4 Results and discussions

4.4.1 Thickness-dependent DC conductivity

Figs. 4.8 and 4.9 show the graphs of the conducting current $I(T)$ vs $1000/T$, as plotted directly by the HP 7475 plotter in the temperature range 573 to 323 K. The plots are approximately linear indicating that the current follows a relationship of the form,

$$I(T) = I_0 e^{-E_a/kT} \quad (4.32)$$

for all films containing 30 at.wt.% Cu and 70 at.wt.% GeO₂ (fig. 4.9) and 100 % GeO₂ (fig. 4.10). I_0 is given by,

$$I_0 = \sigma_0 VA / L \quad (4.33)$$

where σ_0 is a constant, V is the bias voltage, A is the cross-sectional area of the film, L is the length of the electrodes and E_a is the thermal activation energy. The equation above suggests an activated process for the conducting current $I(T)$.

The data in Figs. 4.8 and 4.9, when transformed into conductivity values, yield the $\ln \sigma$ vs $1000/T$ curves as shown in fig 4.10. These graphs clearly show that the conduction process at high temperatures ($T > 323$ K) is best described by the Neugebauer-Webb model (eqn 4.3)

with a negative TCR given by equation (4.4). The thermal activation energy E_a is calculated from the slopes of these curves and have the values 1.08 eV, 1.01 eV and 0.68 eV for 227 nm, 340 nm and 407 nm Cu-GeO₂ films, respectively. For pure GeO₂ film of 395 nm thickness, E_a is found to be 1.17 eV. These values are listed in table 4.1.

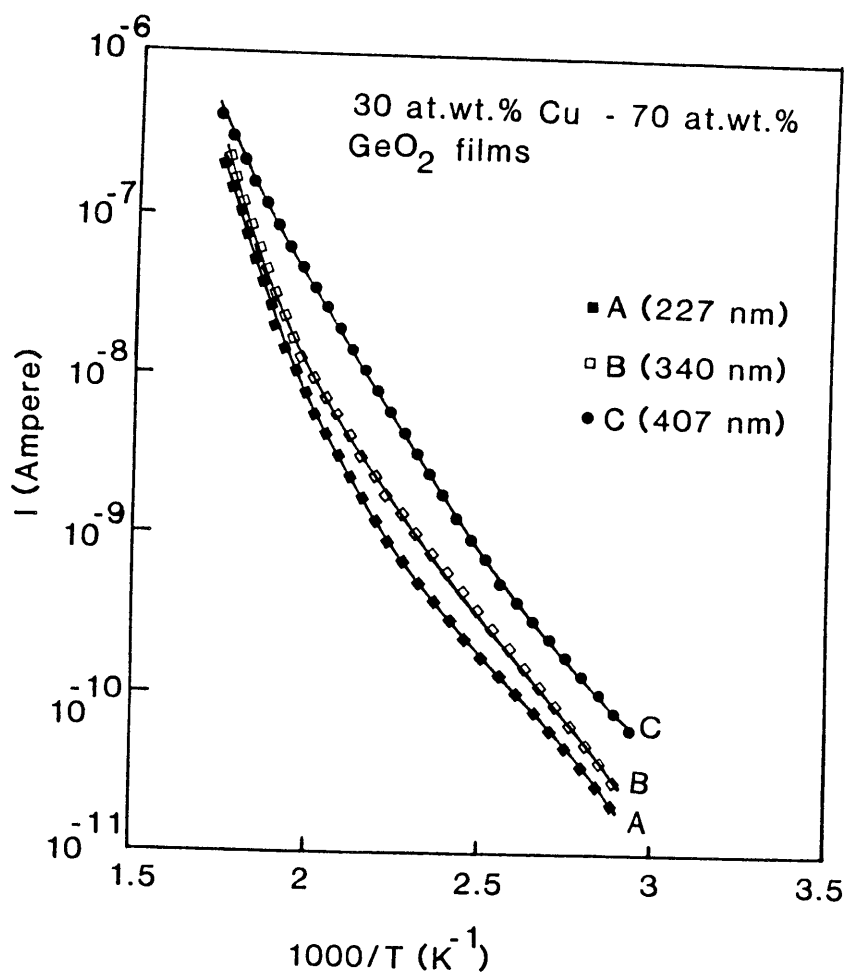


Fig.4.8 Experimental plots of the conduction current $I(T)$ vs $1000/T$ for Cu-GeO₂ films : (A) 227 nm (B) 340 nm (C) 407 nm.

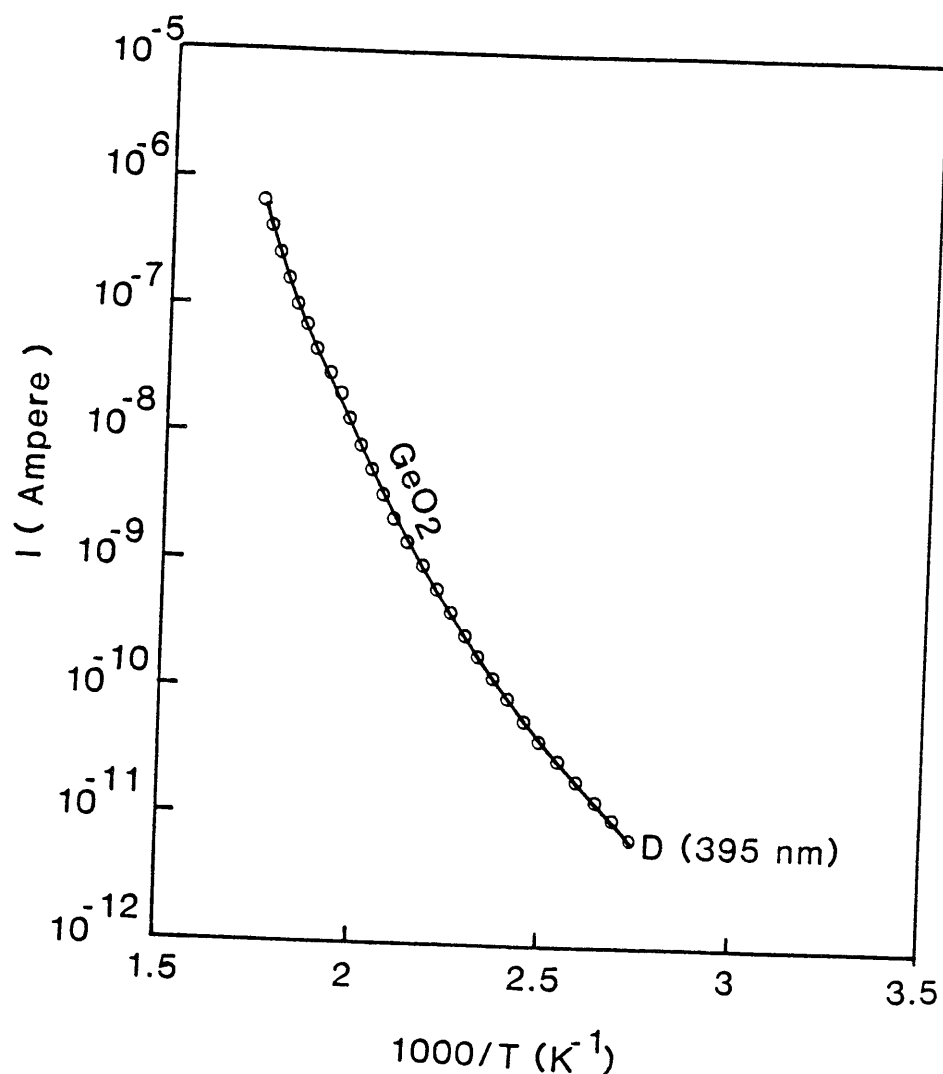


Fig.4.9 Experimental plot of conduction current $I(T)$ vs $1000/T$ for 395 nm thick 100% GeO_2 film.

Table 4.1 Thickness-dependent DC electrical properties of 30 at.wt% Cu-70 at.wt% GeO_2 unannealed films deposited at a substrate temperature of 300 K and at a vacuum pressure of 10^{-3} Pa

Films	Thickness (nm)	Deposition Rate(nm/s)	Activation Energy(eV)	$\sigma_0(\Omega^{-1}m^{-1})$	$\sigma(\Omega^{-1}m^{-1})$ at 323 K
A	227	3.2	1.08	0.6×10^9	8.5×10^{-6}
B	340	2.0	1.01	4.0×10^9	9.8×10^{-6}
C	407	3.1	0.68	2.4×10^6	1.8×10^{-5}
D(GeO_2)	395	3.5	1.17	-	-

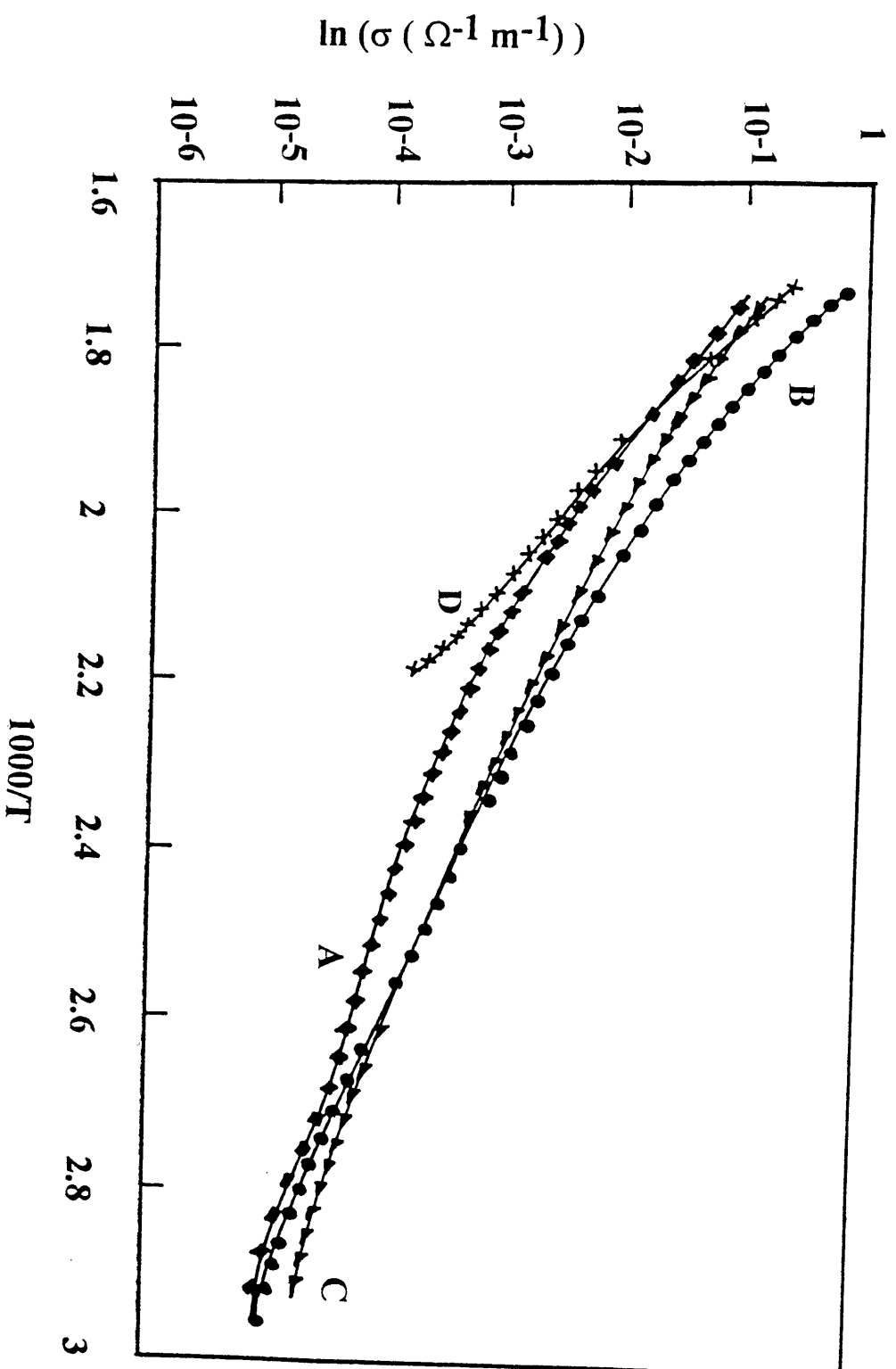


Fig.4.10: Conductivity plotted in accordance with equation (4.3) for the Cu-GeO₂ cermet and 100 % GeO₂ film : (A) 227 nm (B) 340 nm (C) 407 nm (D) 395 nm (GeO₂)

The relatively large values of E_a indicate a strongly activated conduction process, and as a result the conductivity varies over six orders of magnitude in the temperature interval 573 to 323 K. It was also observed that in the high temperature limit ($T \geq 323$ K), the Hill-Coutts model (eqn. 4.6) predicts the same behaviour with n equal to 1. The well-defined single-valued activation energies suggest that the films are discontinuous in nature with metal islands separated by insulating GeO_2 , and that the particle sizes and spacing vary little with temperature. In this case, both the Neugebauer-Webb [1962] and Hill-Coutts [1977] models predict that the overall conductivity will be dominated by charge transport between nearest neighbours and contributions from distant sites can be neglected.

Table 4.1 indicates that the thermal activation energy E_a decreases systematically with increasing film-thickness. Furthermore, comparing E_a for sample C with that of sample D (GeO_2), both of which have approximately the same thickness, suggests that incorporation of Cu in the matrix of GeO_2 has the effect of decreasing the activation energy.

The variation of E_a with thickness can be explained using the Neugebauer-Webb model [1962] in which it is assumed that E_a is proportional to $1/r$, where r is the average linear dimension of a Cu particle. Neglecting the distant-site contributions and assuming that the charge transport occurs between nearest spatial neighbours, E_a is given by e^2/Kr . In the present investigation, thermally activated conduction is assumed to take place between two Cu-islands separated by a space filled with GeO_2 . As the film thickness grows, the space between two islands decreases and the dimension(r) of the islands increases leading to smaller activation energies. Such behaviour was predicted and observed in platinum films

[Neugebauer et al. 1962] triggering the wide spread investigation of this model [Glang et al. 1967, Morris 1972, Schabouska et al. 1986, Al-Saie et al. 1993].

The conduction mechanism in this temperature range can be understood using the results of the optical studies in conjunction with the conductivity data. On comparing E_a with E_{opt} , one can deduce that E_a is less than $1/2 E_{opt}$. This relation indicates that an impurity band, created by the incorporation of Cu particles in the GeO_2 matrix, must exist in the mobility gap. For samples A, B and C, the impurity band would be located at about 1.08, 1.01 and 0.68 eV above (or below, see chapter 5) the Fermi level. Assuming that the Fermi level is midway between the valence and conduction bands, an estimate of mobility gap for the samples can be obtained. For example, the sample C has an E_{opt} of 1.99 eV, hence the mobility gap is calculated to be 2.62 eV.

Morris [1972] and Miller et al. [1970] found that electrostatic charge activated tunneling of carriers through a potential barrier of height 3.7 eV may explain the conduction mechanism in Au-SiO system. On the other hand, for the Cu- GeO_2 system, the barrier height is 2.62 eV for sample C and decreases further for samples A and B. In the present material the mobility gap may not be large enough for the tunneling current to dominate the thermionic current [Simmon 1963]. However, the limiting value of the barrier height below which thermionic emission dominates the tunneling process cannot be determined unless one performs other set of measurements such as thermopower and Hall effect, on the same samples.

Other possibilities of the high temperature conduction mechanism are band conduction and small polaron hopping. The existence of large numbers of localized states are confirmed through optical absorption studies. However,

whether the conduction occurs by carrier hopping through a band of localized states or by carrier excitations from the impurity band across the mobility gap cannot be predicted with definite certainty from the conductivity data alone. Steele and Beynon [1988] report thermally-activated small polaron hopping as the dominant mode of conduction mechanism in Au-SiO films with metallic content 16 at.wt% in the temperature range 333-513 K. Below 333 K, they predict that conductivity may take place by carrier hopping through localized states between Fermi level and the valence band tail.

4.4.2 Composition dependent DC conductivity

The composition-dependent DC conductivity was studied by employing 4-probe technique. The Van der Pauw technique has the advantage that the shape of the sample does not affect the measurements provided the contacts are located anywhere on the periphery. The specific resistivity is given by [van der Pauw 1958]

$$\rho = (\pi t / I 2 \ln 2) [V_{1234} + V_{2314}] f(V_{1234} / V_{2314}) \quad (4.34)$$

where t is the thickness of the sample, I is the measuring current 10^{-9} A, V_{1234} is the potential difference between the contacts 3 and 4 with current passing through contacts 1 and 2, V_{2314} is the potential difference between contacts 1 and 4 with current passing through the terminals 2 and 3. The geometry of the sample is shown in Fig 4.6. The van der Pauw factor f is a function of the voltage-current ratio and can be computed from

$$f(V_{1234} / V_{2314}) = 1 - \left(\frac{V_{1234} - V_{2314}}{V_{1234} + V_{2314}} \right)^2 \frac{\ln 2}{2} - \left(\frac{V_{1234} - V_{2314}}{V_{1234} + V_{2314}} \right)^4 \left\{ \frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12} \right\} \quad (4.35)$$

Since the contacts in the present investigation were symmetrically placed and the samples had approximately uniform thickness (as was observed from transmission

interference fringes), the factor f in equation (4.35) was found to be close to unity and the ratio V_{1234}/V_{2314} , which largely depends on the above two factors, remained almost constant with temperature.

The dependence of conductivity on temperature, calculated using equation (4.34) is shown in fig. 4.11 for all three 410 nm thick samples containing 5, 20 and 30 at.wt.% Cu. It is clear that the slopes continuously change with temperature suggesting that the conductivity σ is an exponentially-activated process with more than a single exponential term to be fitted over the entire temperature range. Furthermore, the conductivity rises sharply beyond a certain temperature T_c . Below T_c the curves gradually level out. For this reason the curves are approximated as two linear regions. Region 1 extends from 307 K to T_c and the conductivity is a weakly-activated process with activation energy E_{a1} . Region 2 on the other hand, extends from T_c to about 413 K. In this region the activation energy E_{a2} shows a remarkable increase over E_{a1} for all the samples marked 1, 2 and 3 respectively as shown in fig. 4.12. Furthermore, above T_c the prefactor σ_{02} (defined in eqn 4.13) increases dramatically by about eight order of magnitude.

It is clear that conductivity changes sharply around the critical temperature T_c suggesting that Nagels' [1973] two-channel model involving simultaneous contributions from two types of carriers may be consistent with the conduction mechanism operating in this material. Such behaviour has been observed in amorphous Si films by Le Comber et al. [1972] and in As-Te-Si system by Nagels et al. [1973]. However, in reality the conductivity curves can not be approximated by two linear regions (see section. (4.4.3)). The values of E_{a1} and E_{a2} , the critical temperatures T_c , the prefactors σ_{01} and σ_{02} , and the resistivity ρ_c at T_c are all listed in table 4.2.

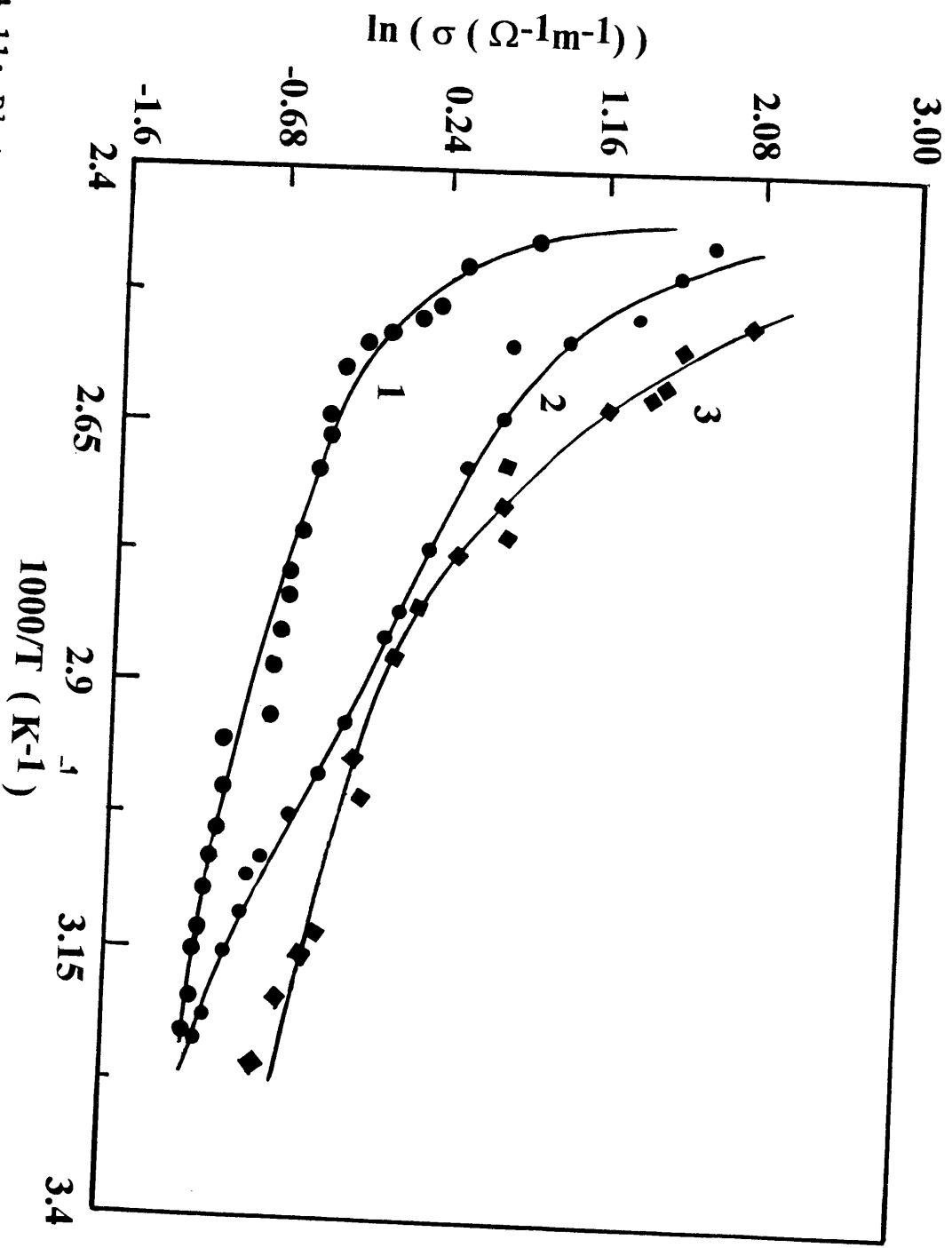


Fig.4.11: Plot of $\ln \sigma$ as a function of $1000/T$ for the Cu-GeO₂ cermets: (1) 5 at.wt.% Cu (2) 20 at.wt.% Cu (3) 30 at.wt.% Cu.

Fig.4.12 Linear regions of the $\ln \sigma$ vs $1000/T$ plot. At $T > T_c$, the activation energy changes from E_{a1} to E_{a2} .

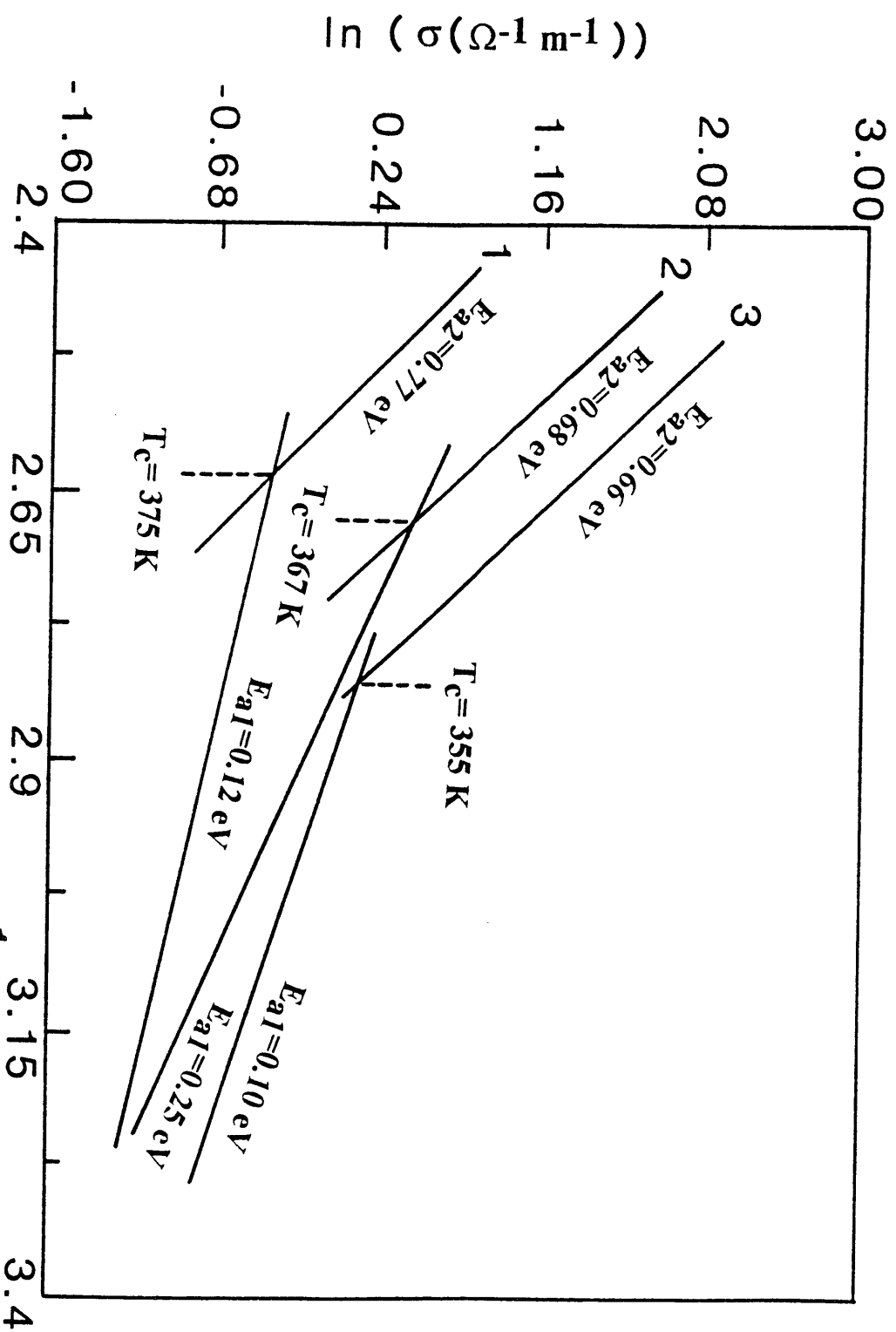


Table 4.2 Conductivity data for Cu-GeO₂ thin films of varying compositions at transition temperature T_C deposited at a substrate temperature of 303 K and a vacuum pressure of 10⁻³ Pa.

Films	Copper content (at.wt%)	T _C (K)	E _{a2} (eV) T>T _C	E _{a1} (eV) T<T _C	σ ₀₂ (Ω ⁻¹ m ⁻¹)	σ ₀₁ (Ω ⁻¹ m ⁻¹)	ρ _c (Ωm)
1	5	375	0.77	0.12	7.8x10 ⁹	22.3	1.53
2	20	367	0.68	0.25	1.1x10 ⁹	2700	0.67
3	30	355	0.66	0.10	2.4x10 ⁹	24	0.63

The shape of $\ln\sigma$ vs $1000/T$ curves (figs. 4.11 and 4.12) strongly suggests that one may be dealing with fundamentally different conduction mechanisms above and below T_C. The considerable increase in E_{a2} over E_{a1}, and σ₀₂ over σ₀₁ at T ≥ T_C lends support to the suggestion that conductivity in region 2 is associated with transport of carriers through extended states. In this case, σ is given by equation (4.12), with E_{a2} = E_C - E_F and σ₀₂ defined by equation (4.13). It is believed that Brownian-type transport (section (4.2.3.2.1)) dominates above T_C where the upper limit of the conductivity mobility is given by equation (4.11). Below T_C, small values of E_{a1} (0.10 to 0.25 eV) and σ₀₁ (22.3 to 2700 Ω⁻¹m⁻¹) indicate that with decreasing temperatures, the probability of thermal release from localized states near E_A or E_B becomes progressively smaller. As a result, it is more likely that the carriers will hop through the spectrum of localized states.

Optical absorption studies (Chapter 3) on Cu-GeO₂ films containing 30 at.wt% Cu (407 nm) indicate that localized states exist with a tail-width of 0.64 eV. Thus, below T_C, it appears that transport of carriers is more likely

to occur by thermally-activated hopping as given by equation (4.14). Equation (4.14) can be rewritten as,

$$\sigma_1 = \sigma_{01} e^{-E_a/kT}$$

where $E_{a1} = E_I - E_F + W$, and σ_{01} is given by equation (4.15), E_I is the impurity level energy and W is the hopping energy between two sites. For 30 at.wt.% Cu film $E_{a1}=0.10$ eV for $T \leq 355$ K and $E_{a2} = 0.66$ eV for $T \geq 355$ K. From these two activation energies, we find that $E_C - E_I = 0.56 + W$. The hopping activation energy W is estimated to be 0.09 eV from the Hall effect measurements on the sample 1 (see section (5.7.1)). Hence, $E_C - E_I = 0.65$ eV. From the optical absorption studies (see section (3.5.2)), the width of the tail states for this sample is $E_C - E_A = E_E = 0.64$ eV. Therefore, the donor impurity states lie about $0.65 - 0.64 = 0.01$ eV below the onset of the tail states. This in turn suggests that one may be dealing with two groups of localized states. The first group resides in the interval $E_C - E_A = 0.64$ eV which originates from the lack of long range order in the material. The second group is localized in the central region between E_A and E_B (near the Fermi level) i.e. 0.01 eV below the tail states which might arise from such structural defects as dangling bonds. Below T_C as the temperature decreases further, the dominant hopping path in the localized state-spectrum seems to move progressively closer to the Fermi level. It should be pointed out that although donor states are associated with a single energy E_I , it is more likely that the donors are distributed in energy throughout the entire tail states [Le Comber et al. 1977]. E_I would then be equivalent to the centroid of the distribution and W would represent some average hopping energy for these states. Noting that room temperature E_{opt} for this sample is 1.99 eV (section (3.5.1)), the mobility gap is calculated to be 3.78 eV.

behaviour of the DC conductivity and Hall mobility in As-Te-Si system, by neglecting the band-tail localized-state's contribution. However, a kink or a sharp transition in the conductivity curves should also trigger similar behaviour in the conductivity and Hall mobility curves [Le Comber et al. 1972, Nagels et al. 1973]. This was not observed in the present work (see section (5.7.1)). In fact, the Hall mobility shows a maximum before decreasing again as the temperature is raised above T_C . This observation together with the fact that the carrier concentration increases sharply beyond T_C (see section (5.7.3)) suggests that at lower temperatures mobility governs the conduction while at higher temperatures ($>T_C$) significant increase in the carrier concentration is responsible for the sudden rise in the conductivity. It will be argued later in Chapter 5 and in the following section that Emin's [1973] small polaron hopping theory best describes the conduction mechanism in Cu-GeO₂ cermet in the temperature range 307 to 413 K.

4.4.3 Variation of activation energy with temperature

A critical look at the conductivity curves (fig. 4.11) shows that the slopes continuously change with temperature, implying the division of the curves into two distinct linear regions may not be adequate. This observation suggests that the activation energy E_a is no longer single-valued and must be evaluated at each point on the curves. The Hill-Coutts model (eqn. 4.9) predicts such behaviour of the activation energy by taking into account the temperature dependence of the size and spacing of the Cu particles. Experimentally, such behaviour was observed in nickel films [Neageuber et al. 1962], Al₂O₃ cermet films [Devenyi et al. 1977], amorphous Si films [Le Comber et al. 1972], Au-SiO films [Morris 1972, Steele et al. 1987, 1988], Cr-SiO films [Schabowska et al. 1986] and in Cu-GeO₂ films [Rahman et

al. 1994]. Devenyi [1977] suggests an empirical relationship to account for this behaviour, viz.

$$E(T) = AT^B \quad (4.36)$$

where A and B are constants and Steele et al. [1988] suggests the following relationship,

$$\sigma(T) = \sigma_0 e^{[-A/kT - B/kT^2]} \quad (4.37)$$

with σ_0 given by,

$$\sigma_0 = eN(E_c)kT\mu_c \quad (4.38)$$

The conductivity σ for a non-degenerate semiconductor can be written as [Jain 1967],

$$\sigma = -e \int N(E)\mu(E)kT \frac{\partial f(E)}{\partial E} dE \quad (4.39)$$

Here $f(E)$ is the Fermi-Dirac distribution of charge carriers, $\mu(E)$ is the effective carrier mobility, $N(E)$ is the density of states per unit volume, per unit energy interval.

Devenyi [1977] and Steele et al. [1987] assumed that the product $N(E)\mu(E)$ in equation (4.39) increases exponentially with energy difference $(E(T) - E_F)$. In this case, the conductivity at an arbitrary energy $E = E_x$ in the tail states can be written as,

$$\sigma = e\mu(E)N(E)e^{\left(-\frac{E_x - E_F}{kT}\right)} \quad (4.40)$$

At lower temperatures, conduction occurs via the localized states near the Fermi level. As the temperature increases, the conduction process moves closer to those states lying further away from the Fermi level. In this case, $E(T) - E_F$ increases suggesting a rapid increase in $N(E)\mu(E)$, and as a consequence, the activation energy increases with temperature.

In this work we concentrate on equation (4.37) where,

$$\ln \sigma = \ln \sigma_0 - (A/kT) - (B/kT^2) \quad (4.41)$$

A temperature dependent activation energy can be defined as

$$E_a(T) = -k \frac{d(\ln \sigma)}{d(1/T)} \quad (4.42)$$

From equations (4.41) and (4.42), one obtains,

$$E_a(T) = A - 2B/T \quad (4.43)$$

Equation (4.43) suggests a temperature-dependent activation energy which increases monotonically with temperature. A least-squares fit of the conductivity data for 5 and 20 at.wt% Cu films using equation (4.41) yields almost straight lines (fig. 4.14). This fit produces the values of the constants A and B and equation (4.43) can be rewritten as,

$$E_a(T) = 2.24 - 634/T \quad \text{for 5 at.wt\% Cu film}$$

and
$$E_a(T) = 2 - 576/T \quad \text{for 20 at.wt\% Cu film}$$

The 30 at.wt.% Cu film does not show a linear behaviour and as such no reliable values of A and B can be obtained. Fig (4.15) shows the variation of $E_a(T)$ with temperature. The almost linear behaviour of the curves indicates that the rate of supply of thermal energy is constant over the entire temperature range. This behaviour indicates that there has not been a sudden increase in the activation energy or an abrupt transition in the conduction mechanism. Therefore, it is believed that the two-channel model or the Mott-type mobility

model does not describe the conduction mechanism appropriately for this material.

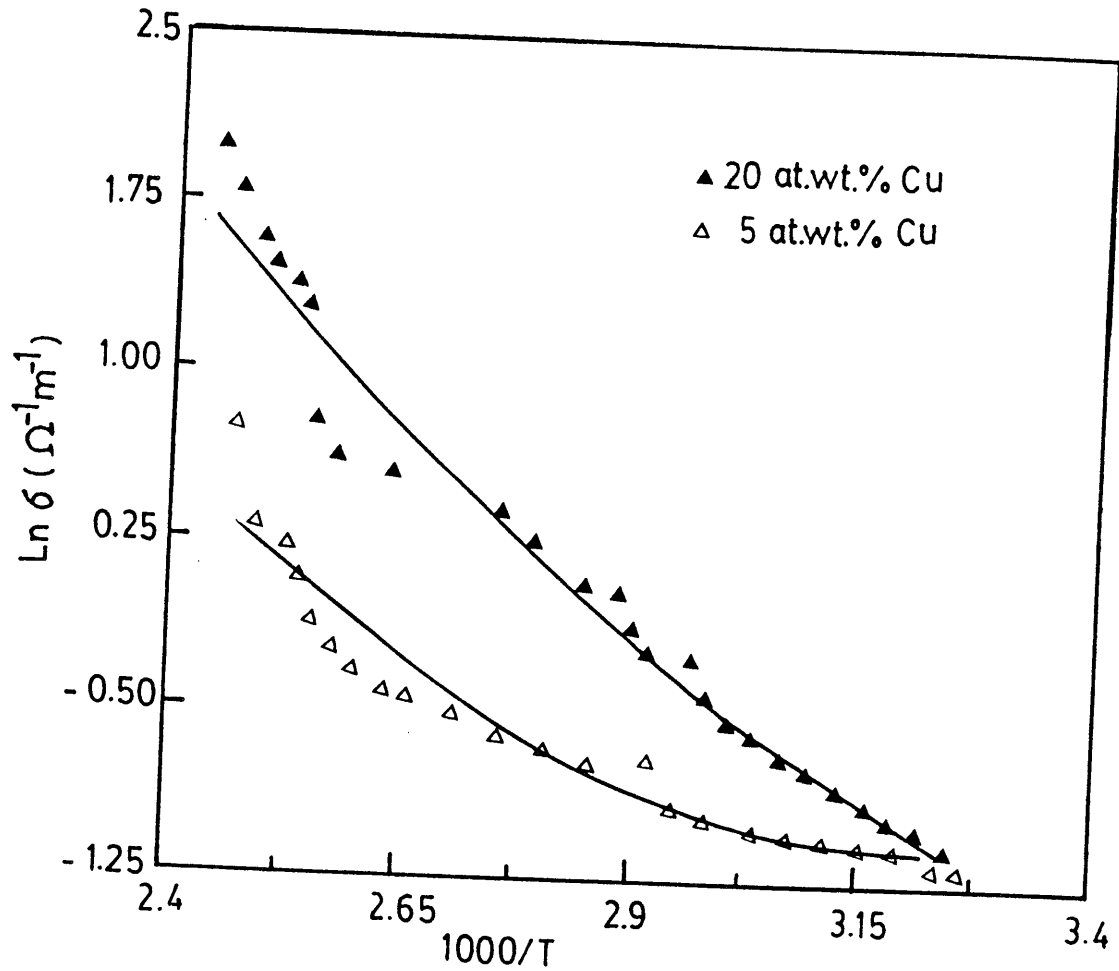


Fig. 4.14: A least-squares fit of the conductivity data in fig.4.11 for 5 and 20 at.wt.% Cu films in accordance with equation (4.41)

Fig. 4.15 shows that E_a increases monotonically with temperature, implying that the maximum current flows at energy $E(T)$ from the Fermi level E_F [Devenyi 1977, Steele

et al. 1987]. According to Devenyi et al. [1977], the monotonic variation of the activation energy with temperature indicates that a mixture of metallic and thermally-activated conduction processes cannot co-exist. Furthermore, the product $N(E)\mu(E)$ must also vary with temperature in a similar fashion, a prerequisite for the determination of the localized states.

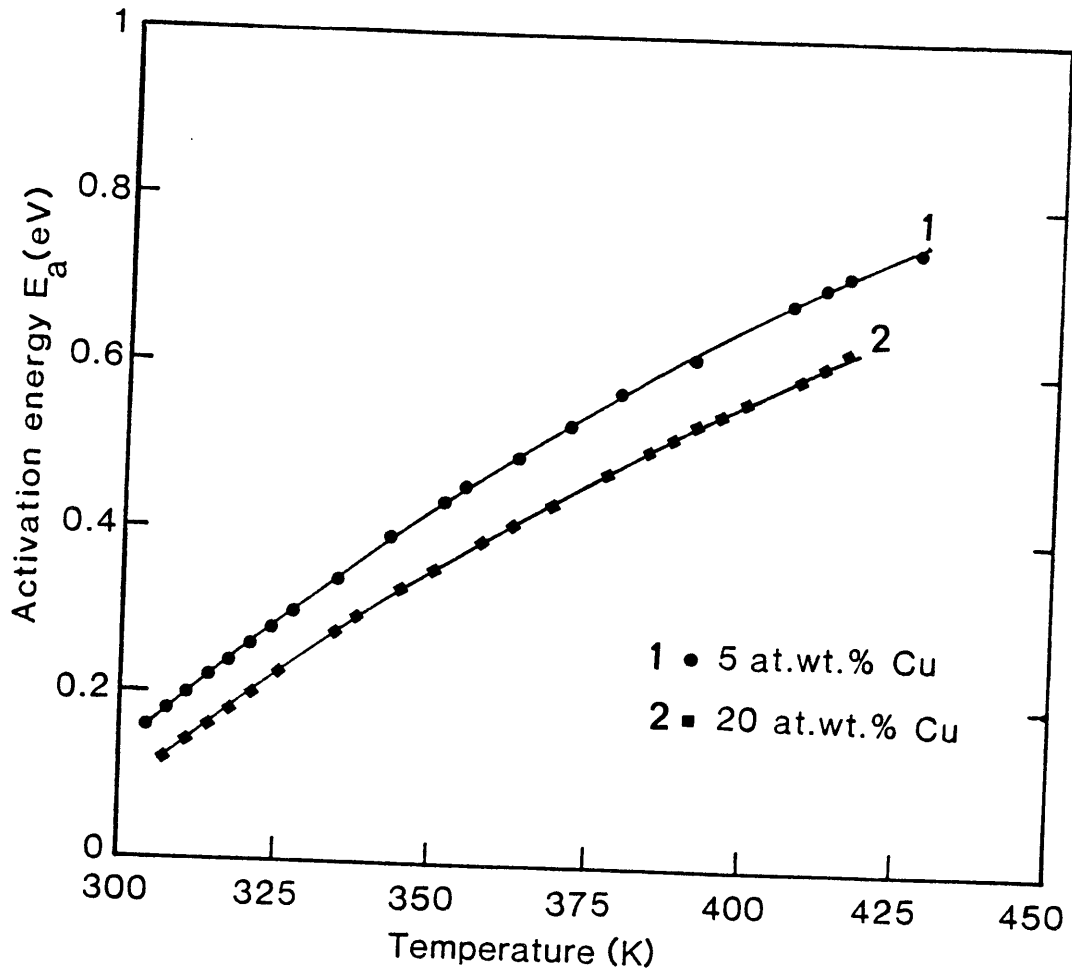


Fig. 4.15: The variation in the activation energy E_a of 5 and 20 at.wt.% Cu films with temperature.

The small polaron conduction mechanism has important signature which can be seen from the equation (4.30) i.e.

$$\sigma = \left(\frac{ne^2}{kT}\right) a^2 P = \left(\frac{ne^2}{kT}\right) a^2 v e^{-W/kT} P_2$$

For $kT \leq W$ i.e. in the lower temperature region, the above equation resembles equation (4.14) i.e. $\sigma_1 = \sigma_{01} e^{-E_{a1}/kT}$ where,

$$\sigma_{01} = (ne^2 a^2 \nu / kT) P_2 \quad (4.44)$$

and

$$E_{a1} = E_A - E_F + W = \varepsilon_0 + W \quad (4.45)$$

According to Emin [1973], ε_0 is the thermal energy needed to produce an equilibrium number of carriers in a disordered material and W is the hopping energy which is expected to have little variation within the same dominant matrix. From the Hall effect measurements (see section (5.7.1)), it has indeed been seen that W remains almost constant (i.e. 0.098 to 0.090 eV) for different samples. Furthermore, since the constants in equation (4.44) also vary little within the same dominant matrix [Emin 1973], σ_{01} is expected to remain constant between the samples. This seems to be the case for samples 1 (5 at.wt% Cu) and sample 3 (30 at.wt.% Cu). The high value of σ_{01} (see Table 4.2) for sample 2 (20 at.wt% Cu) shows considerable dispersion from this predicted behaviour and therefore needs some explanation. Considering the sensitive nature of the experiment in which the conductivity can be effected by all kind of spurious results, there is always a possibility of an experimental error. We attribute this dispersion to the thinner nature of this sample, compared with other two. X-ray fluorescence (XRF) studies reveal that the count rates for the sample 2 (469 CPS) does not show a definite trend relative to samples 1 (447 CPS) and 3 (437 CPS). This observation suggests that the thicknesses of all the samples were not identical. Because of the higher count rates, it is believed that sample 2 is considerably thinner, as a result of which the linear dimension(r) of the Cu-grains will be smaller. This leads to a relatively higher activation energy (0.25 eV).

Furthermore, the smaller dimension of the Cu-grains would also imply that the intersite spacing (a) and the carrier density n in equation (4.44) are considerably larger leading to a significant increase in σ_{01} .

HALL EFFECT AND MAGNETORESISTANCE STUDIES

5.1 Introduction

The temperature-dependences of DC conductivity and Hall mobility yield valuable information about the transport mechanism in amorphous materials. Hall effect studies are the most direct method of studying the temperature effects on free carriers thermally excited from the impurity band. Combining Hall effect with DC electrical conductivity yields the Hall mobility μ_H of the carriers, whilst combining with optical data allows a more substantial understanding of the energy band structure.

DC conductivity results (chapter 4) suggest that the small polaron model best describes the conduction mechanism in the Cu-GeO₂ system in the temperature range 307 to 425 K. Although sufficient experimental data on granular metal films regarding electrical conductivity is available, the Hall effect data are scarce because of experimental difficulties associated with the high resistivity and the very low carrier mobility of the materials. The Hall mobilities of these materials often increase with increasing temperature, and frequently manifest a sign opposite to that of the thermopower. A few works have been published on amorphous semiconductors in which such anomalous behaviour of the Hall mobility have been reported. Early measurements were concentrated on chalcogenide glasses [see reviews by Roilos 1978, Nagels 1979, Mott et al. 1979]. Measurements on As₂Te₃ [Nagels et al. 1973] with a small addition of Si, on amorphous Si:H thin films [Le Comber et al. 1977], on a:Ge [Seager et al. 1974, Lewis 1976] and on some other chalcogenide glasses [Klaffe et al. 1976] reveal some common features; the Hall mobility is very small (10^{-2} to 10^{-1} cm²V⁻¹s⁻¹) and increases slightly with temperature. More

interestingly, the studies mentioned above reported the "anomalous Hall effect" in the sense that the sign of the Hall mobility is opposite to that of thermopower.

Measurements have also been made on a limited number of granular metal films such as Au-SiO₂ and W-Al₂O₃ [Sichel et al. 1982], on Au-SiO_x [Steele et al. 1992] and Cu-GeO₂ [Rahman et al. 1994]. Sichel et al.[1982] reported a sign reversal of the Hall coefficient R_H around the percolation threshold for W-Al₂O₃. Both cermets show R_H to be $\approx 10^{-10}$ m³/C. They attribute the conduction mechanism to be by electronic tunneling between metallic grains. Steele et al.[1992] reported the Hall effect for Au-SiO_x films in the dielectric regime in the temperature range 300-520 K. A sign reversal in R_H was also observed above 400 K but R_H in this case was about 10³ times higher than in Au-SiO₂ [Sichel et al.1982]. The probable cause of the sign reversal in this case was attributed to the conduction mechanism by small polaron hopping.

Interpretation of Hall effect results are usually made in terms of the two-channel model (sections (4.2.4) and (5.4.2)) and the small polaron model (sections (4.2.5) and (5.4.3)). The two-channel model predicts a temperature-dependent Hall mobility which increases with increasing temperature to a constant value. The small polaron model for non-crystalline materials raises serious doubts about the validity of the two-channel model. Significant features of the small polaron hopping motion are that Hall mobility increases with increasing temperature, reaching a maximum, and then decreases with further rise in temperature; the sign of the Hall mobility depends on the nature and geometrical arrangement of the orbitals between which the carrier moves.

In this chapter, Hall effect results obtained on Cu-GeO₂ films (section(5.7.1)) are combined with DC conductivity

results (section (4.4.2)) to obtain further information about the conduction mechanism.

5.2 Hall Effect

5.2.1 Basic concepts

The fundamental or basic idea of the Hall effect is that when a magnetic field is applied perpendicular to the current flow in a material, the current(or the carriers) will be deflected in a direction perpendicular to the original direction of the current and the magnetic field. Let us consider a rectangular shaped semiconductor of width L and thickness t as shown in the fig 5.1. We imagine that a DC current density j_x flows in the x -direction under the influence of an external electric field E_x , applied in the same direction. If a magnetic field B_z is applied along the z -axis, the carriers(say, negatively charged) will tend to deflect towards the negative Y axis creating a Hall field E_y . If v_x is the drift velocity of the carriers in the negative x -direction the deflecting magnetic force will be $e v_x B_z$ acting along the negative Y axis. In the steady-state, $e B_z v_x$ must be balanced by $e E_y$. Thus,

$$e B_z v_x = e E_y \quad (5.1)$$

If the carrier density in the conductor is n , then the current density j_x is given by ,

$$j_x = n e v_x \quad (5.2)$$

Combining equation(5.2) with equation(5.1), one obtains,

$$E_y = (1/ne) j_x B_z \quad (5.3)$$

or

$$E_y = R_H j_x B_z \quad (5.4)$$

where R_H is called the Hall coefficient, given by

$$R_H = (1/ne) \quad (5.5)$$

Equation(5.5) assumes that the carriers are moving with the same uniform velocity v_x which is unrealistic. Depending on the type of scattering of carriers that is dominant, and also the degree of degeneracy in the conduction band, a distribution of velocities may exist. Because of this uncertainty, a factor r is usually introduced in equation(5.5), thus,

$$R_H = (r/ne) \quad (5.6)$$

Generally the factor r does not depart significantly from unity [Putley 1975], and for complete degeneracy, no matter the scattering, one can safely assume r is exactly equal to 1.

The sign of R_H determines the sign of the charge carrier, and knowing R_H , the carrier density n can be effectively determined from equation (5.6). The electrical conductivity σ is given by,

$$j_x = \sigma E_x \quad (5.7)$$

or

$$\sigma = (nev_x/E_x) \quad (5.8)$$

Recalling that $v_x = \mu_c E_x$, where μ_c is the conductivity or drift mobility of the carrier, the conductivity σ can be written as

$$\sigma = \mu_c ne \quad (5.9)$$

Eliminating n between equations (5.6) and (5.9), one obtains

$$R_H \sigma = r \mu_c$$

or

$$\mu_H = R_H \sigma = r \mu_c \quad (5.10)$$

where μ_H is called the Hall mobility. If for simplicity, one assumes the scattering time (τ) to be independent of velocity and that all the carriers possess the same effective mass, then the Hall factor r becomes equal to unity, and

$$\mu_H = \mu_c \quad (5.11)$$

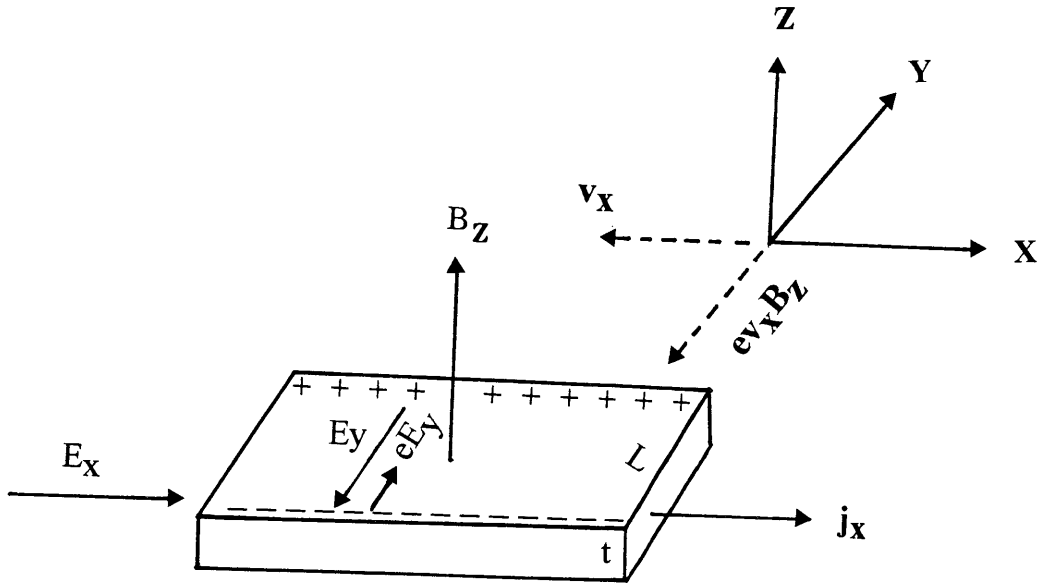


Fig. 5.1: Schematic view of the Hall effect.

Equation (5.11) is valid for carrier motion in a band with a width greater than the thermal energy kT [Emin 1977]. In the case of transport in narrow bands as compared to kT , the states have a high probability of occupancy. As a result μ_H will depend on v_x , the effective mass of the carriers, the energy and the scattering time τ throughout the entire band. In this situation, the Hall factor r will defer from unity

substantially. In fact, for many semiconductor materials r has been found to lie in the range $1 \leq r \leq 2$. Equation (5.5) is based on Boltzmann transport theory of almost free electrons. By applying this theory, Drude was able to develop his free electron theory of conductivity. However, this simple theory could not explain why the carrier concentration in semiconductors is much smaller than in metals and varies rapidly with temperature. To add further confusion to the picture, it was found that in most semiconductors, R_H may be either positive or negative and that the sign of R_H is always opposite to that of the thermopower. This behaviour, totally at variance with that observed in crystalline materials, posed a major challenge to the classical theory of Hall effect. To account for these problems, a quantum theory of conductivity and Hall effect had to be developed. A review of the quantum mechanics-based Hall effect developed by Holstein [1959], Friedman and Holstein [1963] and Emin [1973,1977] is given in section (5.4).

5.2.2 The two carrier expression for R_H

As will be seen in experimental sections (5.7) & (5.8), the Hall coefficient R_H changes sign as a function of temperature. This is an indication that both holes and electrons are present in the Cu-GeO₂ system. In this case, R_H can no longer be given by equation (5.5) and must, therefore, be modified. When both carriers contribute to the overall conductivity, σ is given by

$$\sigma = ne\mu_e + pe\mu_h \quad (5.12)$$

where μ_e and μ_h are the conductivity mobility of electrons and holes respectively. Referring to fig 5.1, the deflection current will now be due to both holes and electrons in the same direction. The deflection current density j_y is given by

$$j_y = epv_{hy} - env_{ey} \quad (5.13)$$

In equilibrium, the above current must be cancelled by σE_y i.e.,

$$\sigma E_y = epv_{hy} - ehv_{ey} \quad (5.14)$$

Here v_{hy} and v_{ey} are the drift velocity of the y-component of the holes and electrons, respectively. Now by definition, the conductivity mobilities of electrons and holes are given by,

$$\mu_{ce} = \frac{e\tau_e}{m} \quad (5.15)$$

and

$$\mu_{ch} = \frac{e\tau_h}{m} \quad (5.16)$$

The conductivity or drift velocity of the holes and electrons in the x-direction are

$$v_{ce} = (\tau_e e E_x / m) \quad (5.17)$$

and

$$v_{ch} = (\tau_h e E_x / m) \quad (5.18)$$

where τ_e and τ_h are the collision times of electrons and holes, respectively. For electrons and holes deflected in the y-direction, equation (5.1) now becomes,

$$ev_{ce}B_z = (mv_{ey} / \tau_e) \quad (5.19)$$

and

$$ev_{ch}B_z = (mv_{hy} / \tau_h) \quad (5.20)$$

Substituting v_{ey} and v_{hy} from equations (5.19) and (5.20) into equation (5.14) and using the definition of μ_{ce} and μ_{ch} one obtains,

$$\sigma E_y = epv_{ch}\mu_{ch}B_z - env_{ce}\mu_{ce}B_z$$

Replacing v_{ch} by $\mu_{ch}E_x$, and v_{ce} by $\mu_{ce}E_x$, the above expression may be rewritten as

$$\sigma E_y = (ep\mu_{ch}^2 - en\mu_{ce}^2)E_x B_z \quad (5.21)$$

Since $E_x = j_x / \sigma$, equations (5.21), (5.12) and (5.4) yield,

$$R_H = (E_y / j_x B_z) = \frac{p\mu_{ch}^2 - n\mu_{ce}^2}{e(p\mu_{ch} + n\mu_{ce})^2} \quad (5.22)$$

However, if collision times τ_e and τ_h are not constant, and if one assumes lattice scattering due to atomic vibrations, then equation (5.22) must be multiplied by the Hall factor r ($=3\pi/8$) [Jain 1967, Putley 1975]. Expressing the ratio of the electron and hole mobilities μ_{ce} / μ_{ch} by b , equation (5.22) can be rewritten as,

$$R_H = (3\pi/8) \frac{p - nb^2}{(p + nb)^2 e} \quad (5.23)$$

It is seen that R_H will pass through zero when p is equal to nb^2 . If the charge carriers are predominantly one type, say holes, then $p \gg n$, and equation (5.23) becomes

$$R_H = (3\pi/8) \frac{1}{pe} \quad (5.24)$$

Equation (5.24) has the same magnitude as equation (5.6) with r equal to $3\pi/8$. We also note that R_H is a function of b if both holes and electrons are present in the material (eqn. 5.23). Hence, sign of the Hall coefficient depends upon the relative mobilities of holes and electrons.

It will be seen in section (5.7) that the sign of the Hall voltage changes with temperature. Equation (5.23) has important implications. According to Putley [1975],

equation (5.23) must be used at intermediate temperatures when holes and electrons from the impurity centres will contribute simultaneously. For materials containing an excess of positive holes, R_H is negative (considering sign anomaly) at lower temperatures. As the temperature is raised, electrons become dominant carriers and the ratio n/p increases. Above a certain critical temperature, R_H will become positive. It must, therefore, pass through zero at some point. Examination of equation (5.23) shows that R_H will pass through zero at $nb^2 = p$. For $nb^2 > p$, R_H will change from negative values to positive values assuming that $b > 1$, which is normally the case. If b is a function of temperature, multiple $R_H = 0$ (i.e sign reversals) is possible. In fact, double reversals of sign have been observed in As_2Te_3 system [Nagels et al. 1973] and in amorphous Si:H thin films [Le Comber et al. 1977]. This behaviour further implies that as the temperature is raised, R_H will pass through a maximum before decreasing (i.e before joining the intrinsic curve).

Equation (5.23) does not show an explicit dependence of R_H on a magnetic field B . This can be obtained by modifying equation (5.23) [Smith 1968]. Assuming that both carriers contribute significantly to the overall current density and that $\tau_e \neq \tau_h$, Smith derives

$$R_H = \frac{(p - nb^2) + b^2 \mu_{ch}^2 B^2 (p - n)}{(bn + p)^2 + b^2 \mu_h^2 B^2 (p - n)^2} \left(\frac{1}{e} \right) \quad (5.25)$$

This equation suggests that R_H will pass through zero when

$$p/n = \frac{b^2(1 + \mu_{ch}^2 B^2)}{(1 + b^2 \mu_h^2 B^2)} \quad (5.26)$$

Equation (5.26) implies that the ratio p/n varies with magnetic field; as the magnetic field is increased, the relative dominance of the carrier concentration will

change, thereby reversing the sign of R_H . Such a sign reversal has been observed in many amorphous semiconductors; in particular it has recently been observed in the Au-SiO_x system in the dielectric regime [Steele et al. 1992].

5.3 Magnetoresistance

Magnetoresistance is the change in resistance of a material in a magnetic field. The reason for this effect lies in the differing mobilities that a carrier may display. If the material possesses only one type of carrier with uniform drift velocity, the carriers will have their Lorentz force exactly balanced by the transverse Hall field. As a result, the magnetoresistance will be zero. This is no longer the case if the material possesses two types of carriers with a distribution of velocities. A large fraction of the carriers may have an average mobility $\bar{\mu}$ (or velocity $\bar{v}$) satisfying the condition for equilibrium. Carriers with velocity or mobility different from the average values will not have their Lorentz forces exactly balanced by the transverse Hall field and, as a result deflection will occur. The deflection will reduce motion in the direction of the applied electric field, thus reducing the effective conductivity or increasing the resistivity.

If ρ_0 is the zero-field (i.e $B_z=0$) resistivity and ρ is the resistivity in the presence of a magnetic field, the magnetoresistance M is defined as [Jain 1967]

$$M = \frac{\rho - \rho_0}{\rho_0} = \frac{\Delta\rho}{\rho_0} \quad (5.27)$$

When both type of carriers contribute to the conductivity, σ is given by equation (5.12) i.e.

$$\sigma = \sigma_e + \sigma_h \quad (5.28)$$

Assuming that the collision times of these carriers are not constant, Jain [1967] derives,

$$M = -\frac{\Delta\sigma}{\sigma} = \frac{\Delta\rho}{\rho_0} = \frac{npb\mu_{ch}^2(1+b)^2}{(nb+p)^2} B_z^2 \quad (5.29)$$

where n and p are the electron and hole concentrations respectively. Equation (5.29) indicates that, provided n, p, μ_{ch} and b remain fairly constant for a material (i.e independent of magnetic field), then $M \propto B_z^2$. The sign of M will be determined by the relative predominance of a particular carrier. Usually in crystalline materials, M is positive for holes and negative for electrons. For non-crystalline materials this distinction is less obvious where the Hall effect arises from a three-site process leading to a sign anomaly. Equation (5.29) also suggests that for unipolar materials with either n or p equal to zero, the magnetoresistance M will be zero. For mixed conduction, M can not be zero.

5.4 Hall effect in amorphous semiconductors

The classical Hall relationships (eqns. 5.6 and 5.10) have been found to be valid for high mobility crystalline materials in which the sign of R_H always equals the sign of the carriers. In low mobility amorphous semiconductors, the mean free path of the carriers is short and comparable to the interatomic spacings, and as a consequence, Boltzmann transport theory cannot be applied. Furthermore, for low mobility transport, the sign of R_H is always opposite to that of the thermopower. In order to understand this anomaly, various quantum mechanics based models have been proposed. The most widely used are the followings:

- a) Random phase model
- b) Two-channel model

c) Small polaron model

5.4.1 Random phase model

This model is based on the assumption that a carrier transition between two sites does not generate a Hall voltage, rather a minimum of a three-site process is needed for that (Fig. 5.2). A three-site process is necessary because, for the hopping situation, the magnetic field-dependence of the jump rates arises from the interference of transition amplitudes of the direct transition (from the initial site to the final one) and the indirect transition via a third site [Holstein 1959, Friedman et al. 1963, Friedman 1971, Emin 1977]. In this model carriers are excited to extended states near the mobility edge where they are assumed to hop between adjacent orbitals. Assuming that the phase of the wavefunctions on the atoms are random, Friedman [1971] calculated the Hall mobility as

$$\mu_H = 4\pi \left(\frac{ea^2}{h} \right) [a^2 J N(E_c)] \eta \left(\frac{\bar{Z}}{Z} \right) \quad (5.30)$$

where J is the overlap energy integral between neighbouring sites; a is the inter-atomic spacings, Z is the coordination number, $\bar{Z}$ is the average number of closed paths about an arbitrary chosen site; η is a parameter related to the three-site path and is usually about equal to $1/3$. Equation (5.30) suggests a temperature-independent Hall mobility for the three-site configuration which is at variance with many experimental observations [Nagels et al. 1973, Mott et al. 1975, Le Comber et al. 1972, 1977, Seager et al. 1975, Vombas et al. 1984, Steele et al. 1992, Rahman et al. 1994].

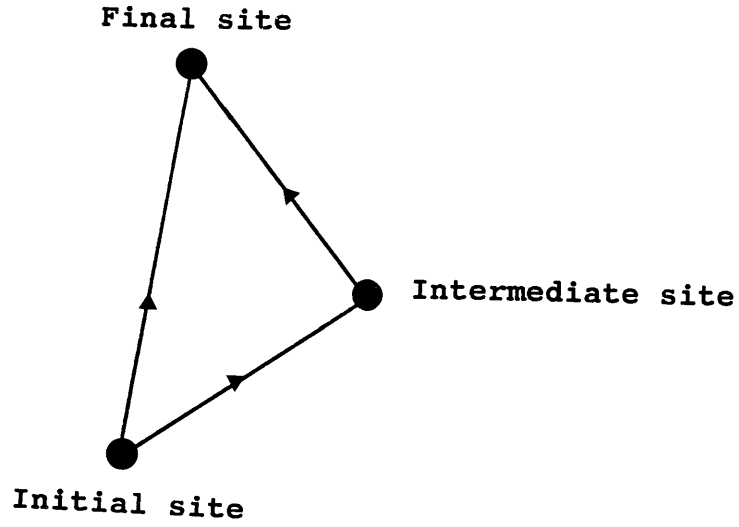


Fig. 5.2: Three site configuration for generating Hall voltage. The sites may be three of the atoms forming a ring in the structure or three of the bonds emanating from a single given atom [Elliot 1990].

Assuming a constant density of states $N(E_c)$, Friedman calculated the dc conductivity σ and the conductivity mobility μ_c as

$$\sigma = \frac{2\pi e^2}{3\hbar a} [za^6 J^2 N(E_c)^2 e^{-(E_c - E_F)/kT}] \quad (5.31)$$

and

$$\mu_c = \frac{2\pi e a^2}{3\hbar} Z \left[\frac{J}{kT} a^3 N(E_c) \right] \quad (5.32)$$

Equation (5.32) suggests that the conductivity mobility decreases with temperature. From equations (5.30) and (5.32), one obtains the ratio,

$$\frac{\mu_H}{\mu_c} = \frac{kT}{J} \quad (5.33)$$

For amorphous semiconductors the Hall mobility μ_H will be considerably smaller than μ_c , since, generally, $J \gg kT$. Friedman calculated this ratio to be 1/10.

This model also predicts an n-type Hall effect for both electrons and holes. The ratio of the signs of R_H for electrons and holes moving in the same band was shown to be equal to $(-1)^{n+1}$. For a three-site process, n is 3. Therefore, both electrons and holes should have the same sign of R_H . This prediction has been found to be inconsistent with many experimental observations in which R_H shows an anomalous behaviour.

5.4.2 Two-channel model

This model has been discussed in chapter 4 (section(4.2.4)) in connection with the dc conductivity in amorphous materials. The random phase model discussed in section (5.4.1) predicts a temperature-independent Hall mobility, while for many amorphous materials, it is found to increase with increasing temperature, and in a few cases, shows a maximum. Nagels et al.[1973] used the two-channel hypothesis to interpret this behaviour. Assuming nearly equal contributions from two competing conducting paths, this model predicts the following:

a) a temperature-dependent Hall mobility which increases with increasing temperature in the lower temperature range($T < 400K$). However, at higher temperatures, carriers are excited to the mobility edge and, consequently, the Hall mobility should become temperature-independent in agreement with the predictions of the random phase model. Since two paths contribute simultaneously to the overall conductivity(see eqn 4.23), the Hall mobility is written as a sum of these two contributions weighted by the total conductivity(see eqn 4.24).

b) The contribution of localised states to the overall Hall mobility is insignificant, in which case the Hall mobility is given by equation (4.25). Furthermore, σ_2 and σ_1 are given by equations (4.12) and (4.14), respectively

in sections (4.2.3.2.1) and (4.2.3.2.2). Substituting these expressions into equation (4.25), one obtains

$$\mu_H = \mu_{H2} \left[1 + \frac{\sigma_{01}}{\sigma_{02}} e^{(E_c - E_A - W)/kT} \right] \quad (5.34)$$

At high temperature, $\sigma_{02} \gg \sigma_{01}$, therefore equation (5.34) reduces to,

$$\mu_H = \mu_{H2} \quad (5.35)$$

Equation (5.35) implies that Hall mobility is totally dominated by the mobility of the carriers in the extended states. An excellent review, in which the validity of this model in a wide variety of materials has been discussed, is given by Nagels [1979].

5.4.3 Small polaron model

The essential features of this model have been discussed in section (4.2.5). It was argued that the conductivity (or drift mobility) μ_c is an activated process increasing exponentially over a broad temperature range (eqn. 4.31) as opposed to the $1/T$ behaviour predicted by the Mott-type band model (eqn. 4.11). The random phase model predicts the same sign for electrons and holes (in non-crystalline materials) whilst the two channel model solves the puzzle by considering almost equal contributions from both carriers, which appears to be unrealistic. Furthermore, the Hall mobility in many amorphous semiconductors has been found to show a maximum before decreasing again in the intrinsic region. The small polaron model for amorphous semiconductors [Emin 1973] attempts to solve the sign anomaly and the behaviour of the Hall mobility by considering not only the local three-site geometry but also the nature and relative orientation of local orbitals between which the carriers move. Consequently, this model eliminates the

concepts of the Davis-Mott type mobility edge and the Nagels' two-channel conduction mechanism.

In this model, in the non-adiabatic approximation, the conductivity mobility is given by equation (4.31). For calculating the Hall mobility μ_H , Friedman and Holstein [1963] considered the charge transfer process in a three-site geometry (Fig. 5.2), and derived an expression for the Hall mobility in the non-adiabatic hopping regime as

$$\mu_H = \frac{ea^2}{\hbar} J \left(\frac{\pi}{12kTW} \right)^{1/2} e^{-W/3kT} \quad (5.36)$$

This equation suggests that the Hall mobility is an activated process with an activation energy one third that of the conductivity mobility μ_c . Furthermore, the pre-exponential term dominates at lower temperatures while the exponential term dominates at higher temperatures. As a result μ_H possesses a maximum at

$$kT = W/3 \quad (5.37)$$

This equation is usually used to calculate the hopping activation energy W .

The ratio of the Hall mobility and the conductivity mobility can be obtained from equations (5.36) and (4.31). Thus,

$$\frac{\mu_H}{\mu_c} = \frac{2}{3\sqrt{3}} \frac{kT}{J} e^{\left(\frac{2W}{3kT}\right)} \quad (5.38)$$

Since $J \gg kT$, equation (5.38) suggests that the Hall mobility is smaller than the conductivity mobility i.e. $\mu_H < \mu_c$. From equation (5.10) we recall that $r = \mu_H / \mu_c$. Using equation (5.6), we now obtain,

$$R_H = \frac{1}{ne}(\mu_H / \mu_e) \quad (5.39)$$

Substituting equation (5.38) into equation (5.39), Friedman et al [1963] obtained the following expression for R_H ,

$$R_H = \frac{2kT}{Jne3\sqrt{3}} e^{(2W/3kT)} \quad (5.40)$$

The behaviour of the pre-exponential and exponential terms as a function of temperature suggests that R_H increases with increasing temperature in the lower part of the temperature range and reaches a maximum at a critical or transition temperature T_C . Beyond T_C , R_H decreases indicating the onset of intrinsic conduction at higher temperatures. By considering the geometry and relative orientation of the orbitals, this model predicts a sign anomaly in R_H in the sense that for hole-like motion it is negative whereas the thermopower is positive. Signatures of this model have been observed in a wide variety of materials and therefore, provide a powerful alternative to band and two channel models.

5.5 Experimental procedure

The film preparation technique and the equipment configuration for van der Pauw conductivity and Hall effect measurements (see fig. 4.6) have been described in sections (4.3.1) and (4.3.3). A photographic view of the set up is given in plate 4. Two external mechanical switches were introduced in the circuit (fig. 4.6) for changing the voltage and current polarities. The magnetic field upto 300 mT was provided by Phewe (West Germany) Hall effect apparatus. The Power supply for the heater and the magnetic field was provided by a stabilised power supply (Farnell L12-10C, 0-12 V, 10 A). A NiCr-NiAl thermocouple was glued to the substrate with the help of

the actual Hall voltage. The application of higher voltages, in order to increase the current through the sample and thus, the Hall voltage, is accompanied by resistive-heating which contributes to offset voltages. To avoid resistive heating and leakage currents, a very low current of 10^{-9} A was used with an accuracy of $\pm 2\%$. The maximum applied voltage was set to 105 within the range of the constant current source Keithley 220. The offset voltage was of the order of mV. Furthermore, this voltage was found to drift with temperature. Special care was then taken to ensure that this offset voltage was eliminated from actual readings. To this end Hall effect measurements were conducted with zero magnetic field and offset voltages noted. Next, with zero current between the electrodes, a cycle of offset voltage was run as a function of temperature. Fig (4.7) shows this variation. Background voltages at each temperature was then normalised in terms of this curve and subtracted from the DMM 195 A readings. Hall voltages obtained in this way were found to be $\approx 10^{-5}$ Volt. The process for eliminating offset voltages will be discussed further in section 5.6.

The Hall effect was investigated on square-shaped samples (dimensions 4 mm x 4 mm) containing 5, 20 and 30 at. wt.% Cu in a static magnetic field of 220 mT. All measurements were confined to the temperature range 307 to 413 K. The experimental limitations did not permit measurements below 307 K and above 425 K.

5.6 Determination of the Hall parameters

In the first set of measurements, the magnetic field B (220 mT) was applied perpendicular to the film-plane. The temperature of the samples was increased to 413 K and readings were taken at 2 minutes interval in descending order at temperatures which correspond to those of the four-probe conductivity measurements (see section

(4.4.2)). The Hall coefficient R_H was obtained by measuring the resulting changes in the voltage. Referring to the equipment configuration in fig.4.6, we draw the following van der Pauw-Hall measurement circuits for the sake of clarity.

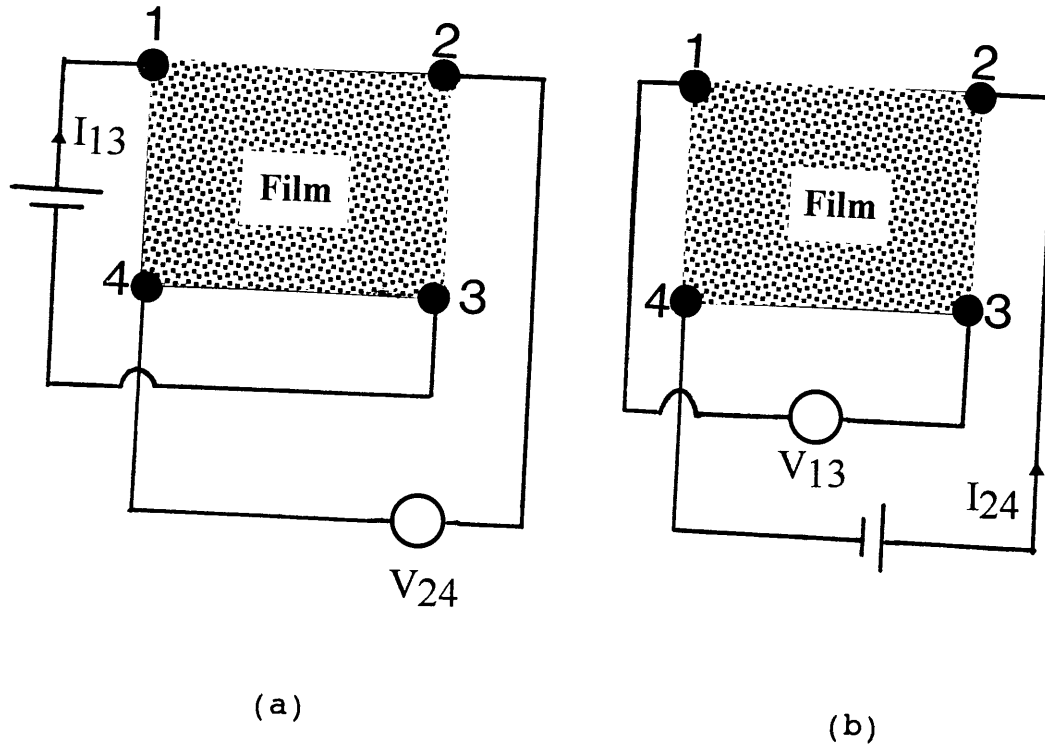


Fig.5.3: van der Pauw-Hall measurement circuits: (a) current applied through the contacts 1 and 3, voltage measured across contacts 2 and 4; (b) current and voltage contacts are interchanged.

From fig.5.3a, R_H can be written as

$$R_H^{(a)} = \frac{t}{B} \frac{(V_{24}(B) - V_{24}(0))}{I_{13}} \quad (5.41)$$

Here I_{13} denotes the current applied through the contacts 1 and 3; $V_{24}(B)$ and $V_{24}(0)$ denote the resulting voltages across the contacts 2 and 4 with B present and absent, respectively. In the second set of measurements current and voltage contacts were interchanged (fig. 5.3b), and

an estimate of $R_H^{(b)}$ was obtained using equation (5.41), with V_{24} replaced by V_{13} and I_{13} replaced by I_{24} . The final R_H was the average of these two measurements, i.e

$$R_H = \frac{R_H^{(a)} + R_H^{(b)}}{2} \quad (5.42)$$

The thermal e.m.f was eliminated by making two measurements on V_{24} and V_{13} with current polarity reversed. With + tive and - tive currents applied, one obtains,

$$V_{24}^+(DMM) = V_{TEMF} + V_{24}^{Real}(sample)$$

$$V_{24}^-(DMM) = V_{TEMF} - V_{24}^{Real}(sample)$$

Here $V_{24}(sample)$ represents the real voltage of the sample in the absence of the thermal e.m.f V_{TEMF} and $V_{24}(DMM)$ is the voltage read by the digital multimeter 195A. Subtracting these two equations yields

$$V_{24}^{Real}(sample) = \frac{V_{24}^+ - V_{24}^-}{2}$$

Similarly, one obtains,

$$V_{13}^{Real} = \frac{V_{13}^+ - V_{13}^-}{2}$$

V_{24} and V_{13} calculated from the above two expressions were used in equation (5.41) to obtain $R_H^{(a)}$ and $R_H^{(b)}$, respectively.

The Hall mobility μ_H was calculated using equation (5.10). Substituting the four-probe expression for ρ (eqn. 4.34) and the Hall coefficient expression R_H (eqn. 5.41) into equation (5.10) gives,

$$\mu_H = \frac{[V_{24}(B) - V_{24}(0)]2 \ln 2}{B \pi f (V_{1234} / V_{2314}) [V_{1234} - V_{2314}]} \quad (5.43)$$

The factor f , which depends on the symmetry of the contacts and homogeneity of the material, was calculated using equation (4.35) and was found to be about 0.96 to 1.0. The carrier concentration n was calculated from the relation

$$n = (1/\mu_H e \rho) \quad (5.44)$$

Knowing ρ and μ_H from equations (4.34) and (5.43) respectively, n can be calculated from equation (5.44).

In the second part of the data collection process, the temperature was kept constant at 303 K, and the magnetic field B was varied in the range 20 mT to 220 mT. This was done in order to calculate the magnetoresistance as a function of magnetic field B . First, following the steps outlined in equations (5.41) and (5.42), the Hall coefficient R_H was found at different magnetic fields. Now the magnetoresistance M is given by equation (5.27) which can be rewritten as,

$$M = \frac{\Delta R}{R_0} = \frac{\Delta V_{24}}{I_{13}} (1/R_0) \quad (5.45)$$

where $\Delta R = R - R_0 = \frac{V_{24}(B) - V_{24}(0)}{I_{13}}$, R is the resistance in the presence of B and R_0 is the resistance in the absence of B . Writing $R_0 = V_{24}(0)/I_{13}$, the above equation becomes,

$$M^{(a)} = \frac{BR_H^{(a)}}{tR_0} = \frac{V_{24}(B) - V_{24}(0)}{V_{24}(0)} \quad (5.46a)$$

Interchanging the current and voltage polarities, one obtains

$$M^{(b)} = \frac{BR_H^{(b)}}{tR_0} = \frac{V_{13}(B) - V_{13}(0)}{V_{13}(0)} \quad (5.46b)$$

The final M was the average of these two i.e.

$$M = \frac{M^{(a)} + M^{(b)}}{2}$$

The magnetoresistance calculated in this way was later plotted as a function of B to investigate the behaviour as predicted in equation (5.29).

5.7 Results and discussions

5.7.1 Hall coefficient and Hall mobility

The Hall voltage was recorded to be $\approx 10^{-5}$ V for all the three samples. R_H was calculated from equations (5.41) and (5.42) in the temperature range 307 to 413 K for a constant magnetic field of 220 mT; the values all lie in the range $-400 \times 10^{-3} \text{ m}^3 \text{ C}^{-1}$ to $320 \times 10^{-3} \text{ m}^3 \text{ C}^{-1}$. Fig. 5.4 shows the variation of R_H with substrate temperature. A sign reversal of the Hall coefficient was observed for all the samples. For samples 1 and 2, containing 5 and 20 at.wt.% Cu, respectively, R_H is negative in the lower part of the temperature range. Above 335 K and 323 K, respectively, R_H becomes positive, reaching a maximum and then continues to decrease slowly. Sample 3 (30 at.wt.% Cu) exhibits a positive R_H ($160 \times 10^{-3} \text{ m}^3 \text{ C}^{-1}$ at 307 K) which increases with increasing temperature upto a maximum at 331 K. Above 331 K, R_H decreases rapidly compared to that observed in other two samples, becoming negative above 389 K: $R_H \approx 10^{-3} \text{ m}^3 \text{ C}^{-1}$. These values are rather large compared to the known values of other cermet materials in the dielectric regime; a factor of 10^3 times higher than observed in Au-SiO_x films [Steele et al. 1992], 10^7 times higher than in W-Al₂O₃ cermets [Sichel et al. 1982] and 10^6 times higher than in Au-SiO₂ films [Sichel et al. 1982]. As can also be seen from fig. 5.4, the magnitude of R_H increases with increasing copper contents for all temperatures upto 380 K.

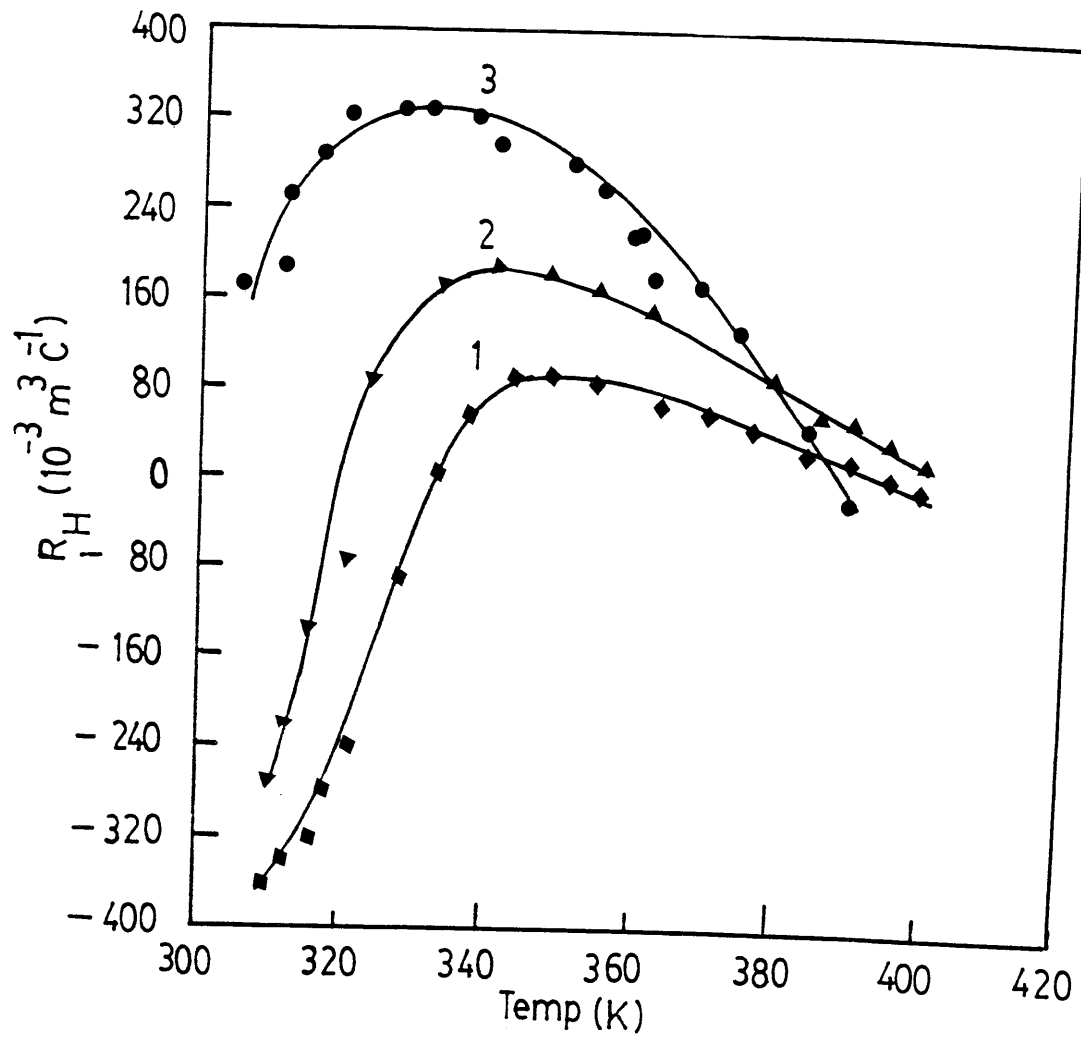


Fig.5.4: Temperature dependence of Hall coefficient R_H at a magnetic field of 220 mT for Cu-GeO₂ films: (1) 5 at.wt.% Cu; (2) 20 at.wt.% Cu; (3) 30 at.wt.% Cu.

Using equation (5.43), the Hall mobility μ_H was calculated to be $\approx 10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility is about 10 times higher than in Au-SiO_x films [Steele et al. 1992], about 100 times higher than in chalcogenide glasses [Seager et al. 1973,1975; Nagels et al. 1973], about 100 times higher than in a:Si [Le Comber et al. 1977, Reilly et al. 1978], but comparable with n-type MnO [Dewit et al. 1967].

Graphs of μ_H vs T (fig. 5.5) exhibit two distinct temperature regions similar to those for the conductivity curves (figs. 4.11 and 4.12). The curves have maxima at critical temperatures 375, 367 and 355 K for samples 1, 2 and 3, respectively. Above these temperatures, μ_H decreases slowly with increasing temperature. Values of R_H and μ_H at critical temperatures T_c are listed in Table 5.1.

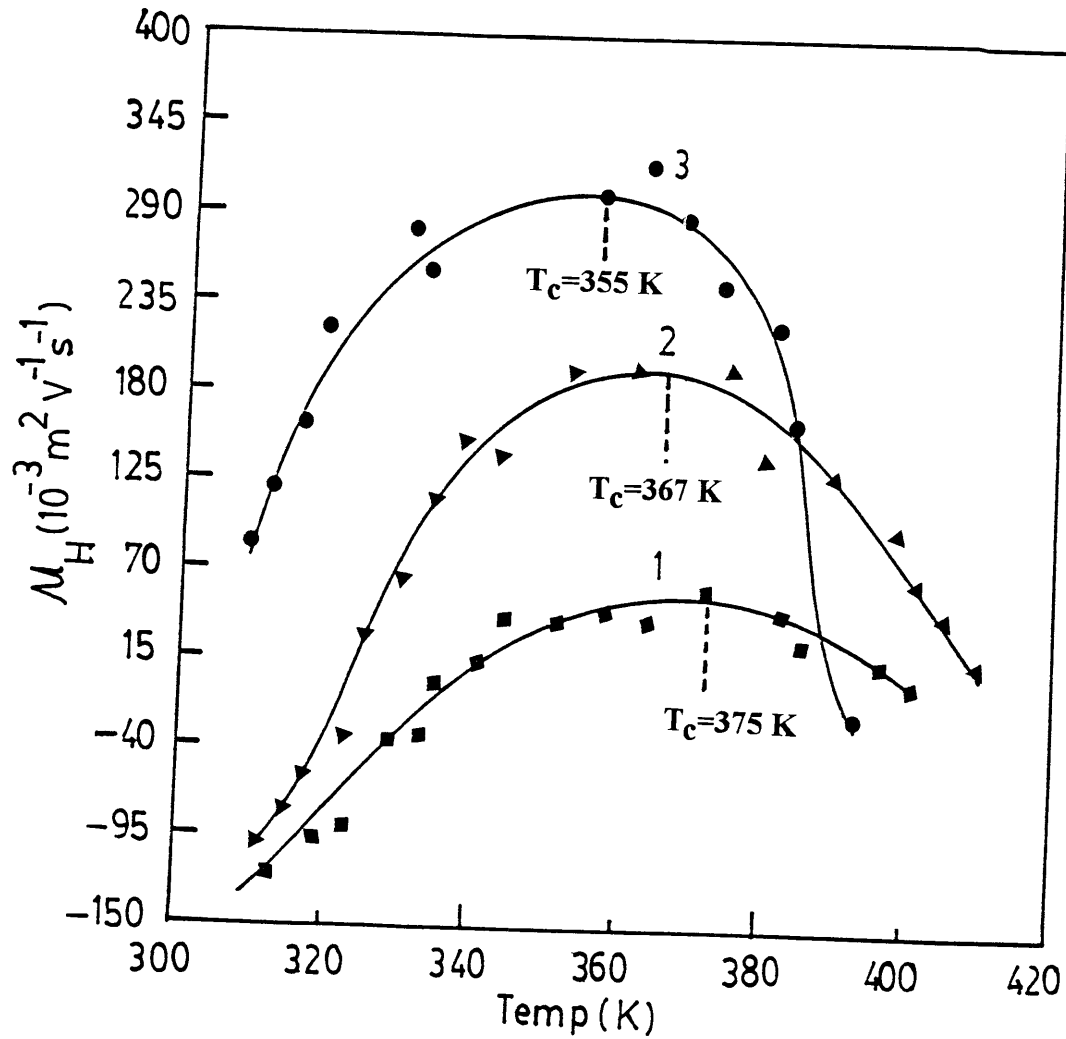


Fig.5.5 : Temperature dependence of Hall mobility μ_H at a magnetic field of 220 mT for Cu-GeO₂ films: (1) 5 at.wt.% Cu; (2) 20 at.wt.% Cu; (3) 30 at.wt.% Cu.

The fact that the conductivity and mobility critical (or transition) temperatures are identical indicates that there exists a fundamental difference in the transport

properties below and above T_C . This notion is further supported by the conductivity curves (figs. 4.11 and 4.12) which show a gradual increase in conductivity in the lower temperature range, but a rapid rise above T_C . The change in sign of R_H that occurs as temperature increases and the maximum in μ_H at T_C may also imply that the conductivity in Cu-GeO₂ thin films results from a combination of two processes. This suggests that both n and p type carriers are present in the material and the behaviour of R_H is described by the equations (5.23) and (5.25). Depending on the relative mobilities of these two carriers, these equations predict the sign reversal in R_H observed in the present work.

The two channel-model (section 5.4.2)) predicts a change in conduction from localized states to extended states as the temperature is raised above T_C and an increase in Hall mobility μ_H with increasing temperature to a constant value (as was also predicted by Random phase model eqn. 5.30). This is in marked contrast to the observed behaviour of R_H and μ_H in the present work (see figs. 5.4 and 5.5), both of which show a maximum. Therefore it is very likely that the small polaron model (section 5.4.3)) best describes the conduction mechanism in this material. A similar behaviour was also observed in Au-SiO_x cermet [Steele et al. 1992].

The temperature dependence of the pre-exponential and exponential terms in equations (5.36) and (5.40) produce a maximum in the mobility and Hall coefficient, respectively, in agreement with figs. (5.5) and (5.4). At $kT = W/3$, the mobility reaches a maximum, from which W may be calculated to be 0.098, 0.095 and 0.090 eV for samples 1, 2 and 3, respectively, as listed in Table 5.1. These compare favourably with those obtained with Au-SiO_x films (0.090-0.10 eV, Steele et al.1992). Low values of the hopping energy W , in the range 0.06 - 0.08 eV, have been

reported for As-Te based glasses [Seager et al. 1975], and for a:Si [Lecomber et al. 1977]. Such low values of W characterize a low mobility, and is one of the consequences of the small polaron hopping theory. As W in amorphous materials is mostly determined by the disorder potential introduced by GeO_2 , and since GeO_2 remains a dominant matrix for all the samples, one would expect W to vary little between the samples. Another prediction of the small polaron hopping theory is that the prefactor σ_{01} in equation (4.44) should also vary little within the same dominant matrix [Emin 1973]. As explained in section (4.4.3), samples 1 and 3 conform to this prediction. The discrepancy in the value for sample 2 is largely attributed to the uncertainty in film thickness.

For 5 and 20 at.wt.% Cu films, R_H starts from a negative value at room temperature but becomes positive above 335 K and 323 K, respectively. Considering the sign anomaly due to the three-site hopping process [Friedman and Holstein 1963, Emin 1973], this result implies that holes make the major contribution to the conductivity for $T \leq 335$ K and $T \leq 323$ K, respectively, in the two samples. Above these temperatures, the conductivity is dominated by electrons. Therefore, the conductivity below the critical temperature (e.g. 375 and 367 K) in these samples is dominated by a mixed conduction process and equation (5.23) must be used to discuss the behaviour of R_H .

When the temperature rises beyond T_C , R_H passes through a maximum and intrinsic conduction sets in. In the intrinsic region, mobility decreases (fig. 5.5) but conductivity increases sharply (fig. 4.11), with the result that carrier concentration must increase significantly in the intrinsic region. The magnitude of R_H in the high temperature region indicates that n increases by about 100 times as the temperature is raised above T_C . Also, the thermal agitation of lattice atoms

increases and the collision rate increases. Such lattice scattering is believed to be responsible for the decrease in mobility at higher temperatures. Hence, it is believed that in the intrinsic region, carrier concentration will govern the conductivity and mask the effects of mobility.

In the extrinsic region (i.e $T < T_C$), the Hall mobility has a high negative value initially, the magnitude of which slowly decreases to zero as temperature rises. This implies that around room temperature, the material has an excess of positive holes. As the temperature rises towards 335 and 323 K for the two samples, respectively, the number of holes decreases and the number of electrons increases. Because of the changing relative proportions of the carriers, R_H and μ_H both pass through zero, as predicted by equations (5.23) and (5.36). The mobility shows a rapid rise as the temperature increases to T_C while the relatively larger values of R_H in this temperature region suggests a weaker increase in carrier concentration n . This, together with the fact that the conductivity in this temperature region is weakly activated (see section (4.4.2)), implies that mobility governs the conduction mechanism.

For sample 3 (30 at.wt.% Cu film), R_H is positive up to 389 K. This clearly indicates that electrons are the major contributors to the conductivity. This further suggests that with increasing Cu content, mixed conduction diminishes and the material tend to become unipolar.

Between 389 and 413 K, values of R_H are negative. Below T_C (<355 K) the small value of the thermal activation energy of 0.10 eV, (see section (4.4.2)) suggests that conduction occurs by carrier hopping through localized states, while above 355 K, a sudden jump in the activation energy (0.66 eV) suggests that transport of

electrons occurs via extended states above E_c . A knowledge of the tail-width of the localized states (see section (3.5.2)), the thermal activation energies (section (4.4.2)) and the hopping activation energy W for this sample has already been used in section (4.4.2) to determine the position of the donor states relative to the Fermi level (see fig. 4.13). This will not be discussed further.

Table 5.1 Data for Hall effect measurements near transition temperature T_c at a magnetic field of 220 mT.

Cu-content (at.wt.%)	T_c (K)	μ_H ($10^{-3}m^2V^{-1}s^{-1}$)	R_H ($10^{-3}m^3C^{-1}$)	W (eV)	$n(m^{-3})$
5	375	36	55	0.098	11×10^{19}
20	367	198	133	0.095	4.7×10^{19}
30	355	308	194	0.090	3.2×10^{19}

5.7.2 Magnetoresistance

Magnetoresistance M was calculated using equations (5.46a) and (5.46b). The magnitude of M lies in the range 5×10^{-3} to 4.5×10^{-1} corresponding to the magnetic field range 20 mT to 180 mT, as shown in fig. 5.6. For sample 1, M was found to be negative at room temperature, 303 K, lying in the range 9.0×10^{-4} to 7.5×10^{-2} . The magnitude is seen to increase with increasing B . For sample 2, M is also negative, magnitude increasing with B in the range 1.0×10^{-4} to 3.0×10^{-1} . For sample 3, M is positive increasing with B in the range 1.2×10^{-3} to 4.1×10^{-1} . The sign of M is consistent with the signs of R_H and μ_H . Furthermore, M is seen to increase with increasing Cu-contents (see fig. 5.6). Below a B of 40 mT, a substantial amount of noise was present, and consequently, some degree of uncertainty exists in the

accuracy of the results. M saturated above 180 mT for samples 1 and 3.

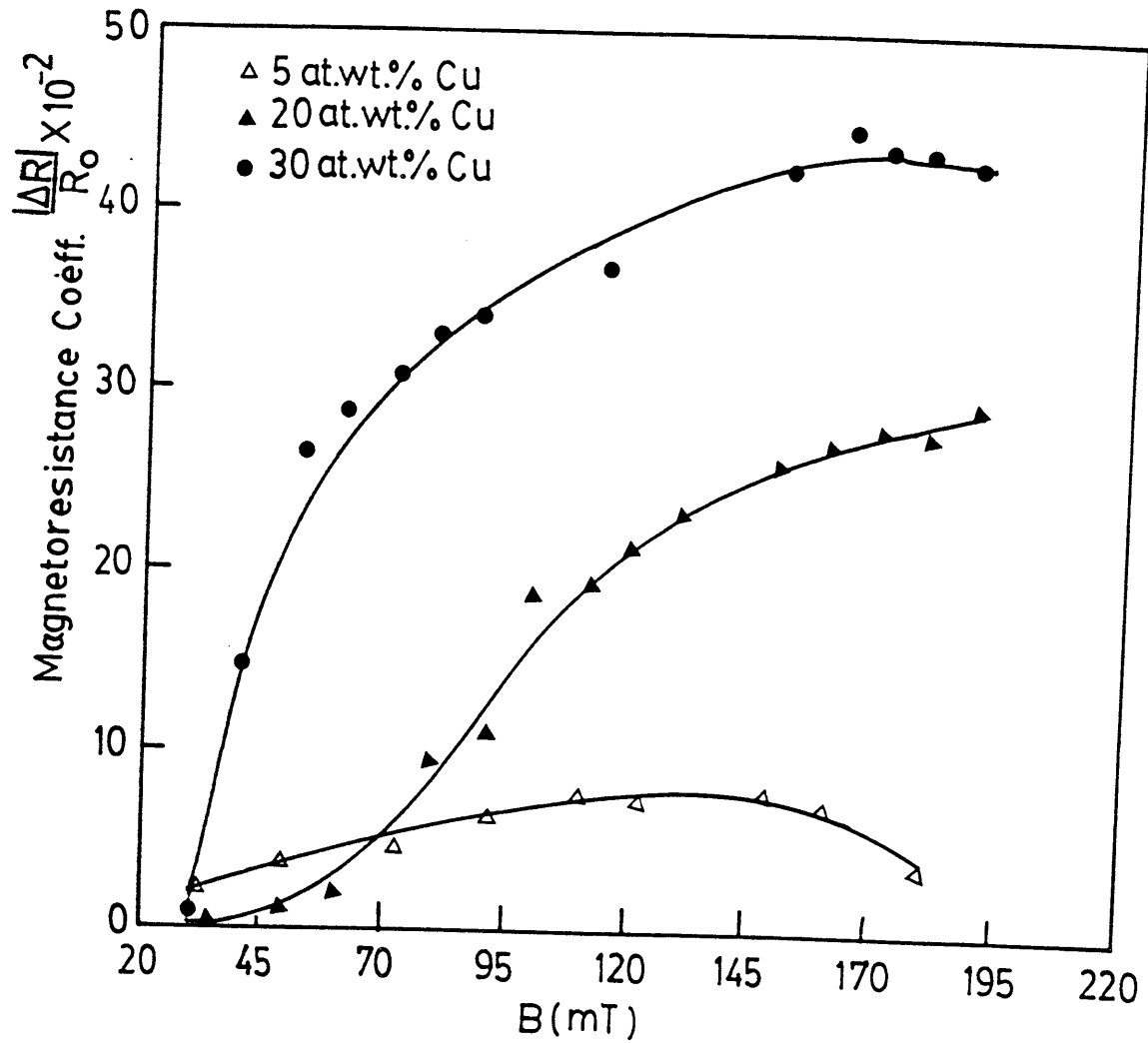


Fig.5.6: Magnetoresistance (M) as a function of magnetic field (B) at 303 K for Cu-GeO₂ films.

Because a mixed conduction process has been established in the material below the critical temperature, it appears that the behaviour of M should be governed by equation (5.29), i.e $M \propto B^2$. However, if it is assumed that n, p, μ_{ch} and b are practically independent of B , the equation(5.29) can be rewritten as

$$M = AB^n \quad (5.47)$$

where

$$A = \frac{npb\mu_{ch}^2(1+b)^2}{(nb+p)^2}$$

A $\ln M$ vs $\ln B$ graph (fig. 5.7) yields n to be 1.63 for sample 1, 2.44 for sample 2, and 2.10 for sample 3. These values are in reasonable agreement with $n \approx 2$ behaviour predicted by equation (5.29).

Considering the sign anomaly, the negative values of M indicates hole conduction via localized states, while the positive values of M are a consequence of electron conduction. Mell and Stuke [1970] interpret the negative magnetoresistance as indicative of a hopping mechanism near the Fermi level. As the temperature increases, conduction switches from localized states to extended states where a positive R_H is expected. This is observed in samples 1 and 2. A similar interpretation applies for sample 3 but in this case the predominant carriers are electrons below T_C and holes above T_C .

The mixed conduction process offers some explanation for the observed negative M in samples 1 and 2. Substituting equation (5.28) into equation (5.29) gives,

$$M = -\frac{\Delta\sigma}{\sigma} = -\left(\frac{\Delta\sigma_2 + \Delta\sigma_1}{\sigma_2 + \sigma_1}\right) \quad (5.48)$$

Conductivity data in fig. 4.11 shows that extended-state conductivity is about 100 times greater than localized state-conductivity; in which event contribution from localized states to the overall conductivity can be neglected. Hence, equation (5.48) becomes,

$$M = -\frac{(\Delta\sigma_2 + \Delta\sigma_1)}{\sigma_2} \quad (5.49)$$

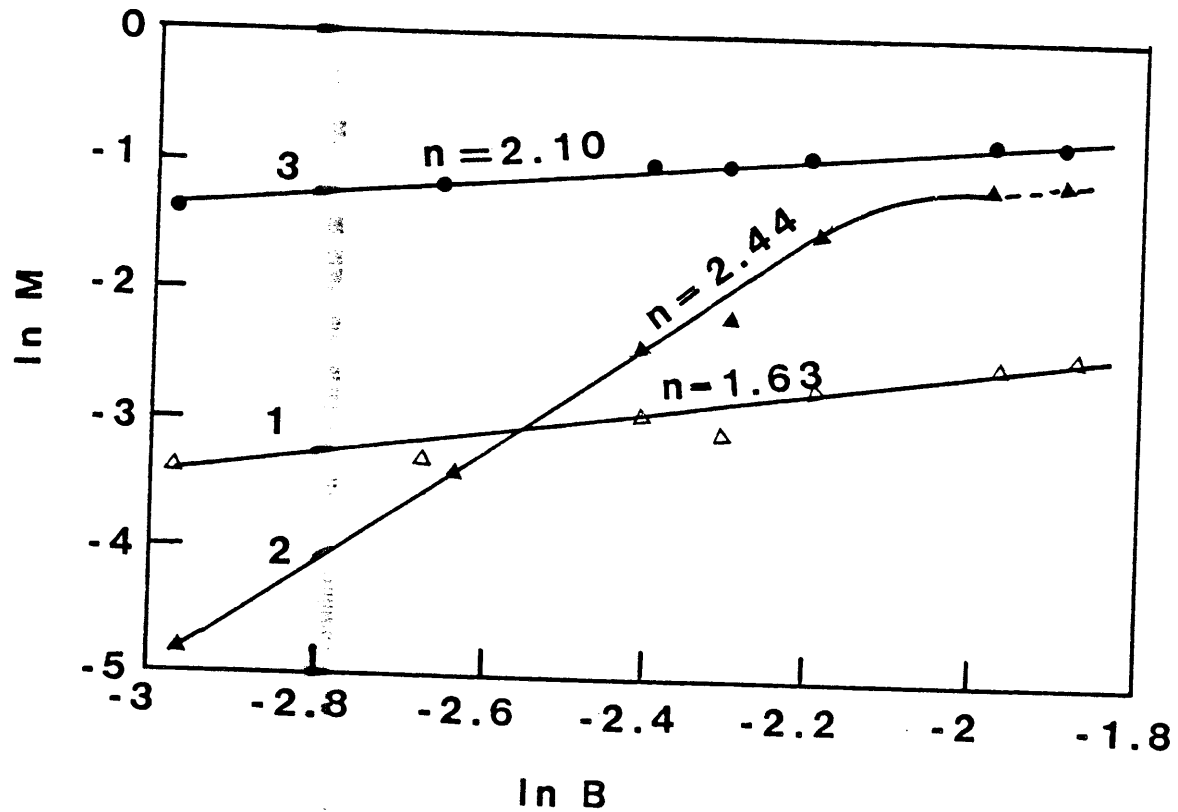


Fig.5.7: $\ln M$ vs $\ln B$ plots for Cu-GeO₂ films (in accordance with equation (5.47)): (1) 5 at.wt.% Cu; (2) 20 at.wt.% Cu; (3) 30 at.wt.% Cu.

Now the major effect of a magnetic field is to align spins associated with impurity sites (or carriers) in such a way that a hopping carrier can easily occupy that site without violating Pauli's Exclusion Principle [Mell and Stuke 1970]. In this case, the probability of hopping to an empty site will increase i.e. $\Delta\sigma_1 \gg \Delta\sigma_2$. Equation (5.49) then becomes,

$$M = -\frac{\Delta\sigma_1}{\sigma_2} \quad (5.50)$$

This equation suggests a negative M arising from the hopping conduction mechanism through impurity states, in agreement with experimental observations on samples 1 and 2.

5.7.3 Intrinsic conduction

The form of conductivity (fig. 4.11), Hall coefficient (fig. 5.4) and mobility (fig. 5.5) curves suggests that above T_c impurity carriers may be ignored, resulting in intrinsic conduction. To confirm this possibility, the carrier concentration n was calculated using equation (5.44) and was found to lie in the range 10^{19} to 10^{21} m^{-3} for the temperature range 307 to 425 K. The values of n near T_c is listed in Table 5.1. All of the three samples show that for $T > T_c$, n increases 100 fold, i.e from 10^{19} to 10^{21} m^{-3} . In the intrinsic region, ignoring the impurity carriers, the intrinsic carrier concentration n_i may be written as [Smith 1968, Putley 1975],

$$n_i = 2\left(\frac{2\pi k}{h^2}\right)^{3/2} (m_e^* m_h^*) T^{3/2} e^{-E_a/kT}$$

or

$$n_i = AT^{3/2} e^{-E_a/kT} \quad (5.51)$$

where

$$A = 2\left(\frac{2\pi k}{h^2}\right)^{3/2} (m_e^* m_h^*)^{3/4} \quad (5.52)$$

Here m_e^* and m_h^* are the effective masses of electrons and holes, respectively. Since n_i (or p_i) is known from Hall effect measurements, equation (5.51) can be used to determine the high temperature activation energy E_a , m_e^* and m_h^* . One test of intrinsic conduction is to compare

E_a , thus found, to that obtained from the conductivity curves in fig. 4.11.

From equation (5.51), one obtains,

$$\ln(n_i T^{-3/2}) = \ln A - E_a / kT \quad (5.53)$$

A and E_a may now be determined from the intercept and gradient of a graph of $\ln(n_i T^{-3/2})$ vs $1000/T$ (see fig.5.8). m_e^* and m_h^* may then be calculated from the values of A if it is assumed that they are equal. These values are listed in Table 5.2.

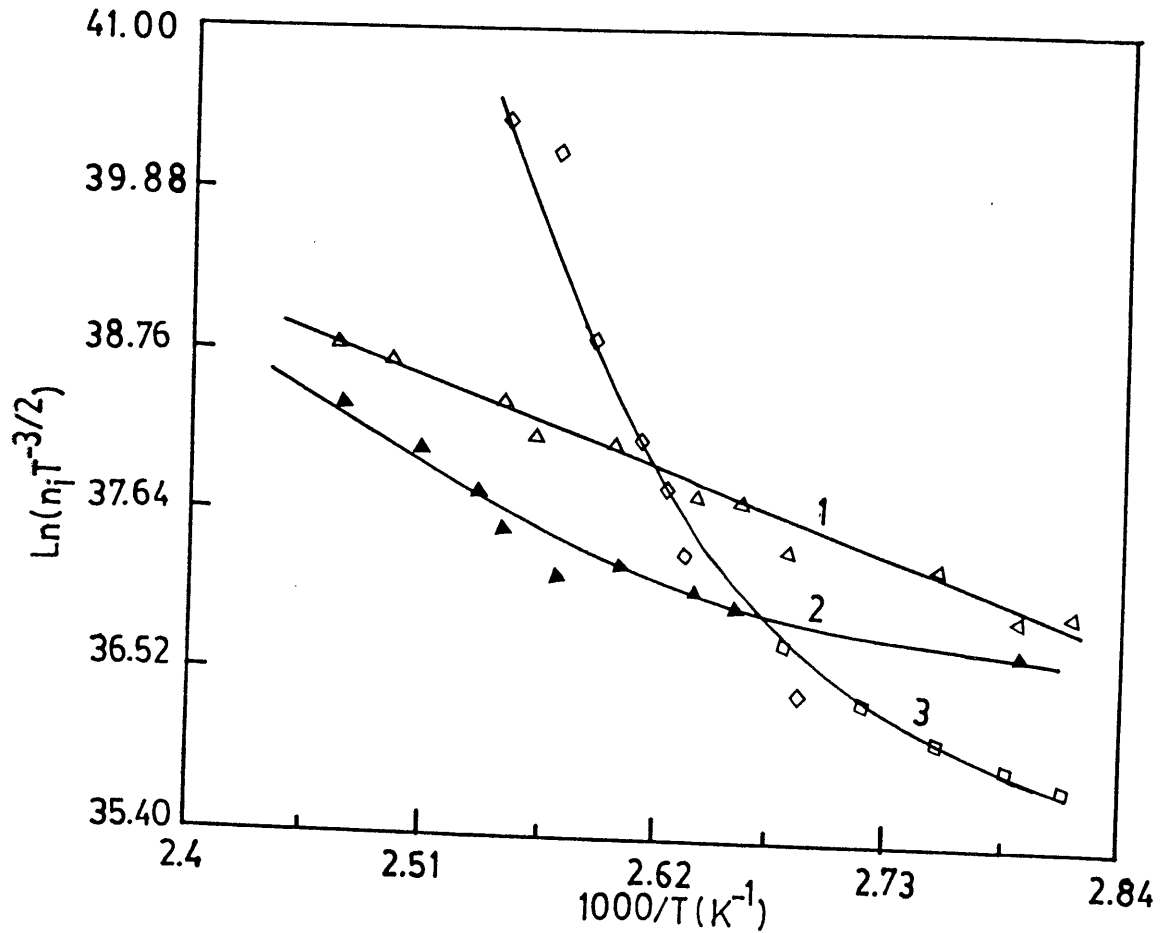


Fig.5.8: Variation of $\ln(n_i T^{-3/2})$ with $1000/T$ for Cu-GeO₂ films in accordance with equation (5.53): (1) 5 at.wt.% Cu; (2) 20 at.wt.% Cu; (3) 30 at.wt.% Cu

Table 5.2 Values of A , E_a , m_e^* and m_h^* obtained from the intrinsic curves ($T > T_c$, fig. 5.8) assuming $m_e^* = m_h^*$

Films	$A(m^{-3}K^{-3/2})$	$E_a(eV)$	$m_e^* = m_h^*$
1(5% Cu)	6.94×10^{24}	0.70	$100 m_e$
2(20%Cu)	6.00×10^{24}	0.65	$100 m_e$
3(30%Cu)	5.00×10^{24}	0.66	$100 m_e$

Activation energies calculated from the conductivity curves (fig. 4.11) were 0.77, 0.68 and 0.66 eV for samples 1, 2 and 3, respectively. There is a remarkable agreement with the activation energies obtained from the intrinsic curves (fig. 5.8). However, there are some problems with this method of obtaining the activation energy. As seen from fig. (5.8), the curves are not entirely linear. This small curvature arises because the high temperature activation energy E_a is not constant but, rather, depends on temperature, as explained in chapter 4 (section (4.4.3)). In addition, the Fermi energy E_F may itself shift with temperature [Smith 1968]. Both of these variations introduce significant errors into the results. However, as seen from fig. (5.8) the curvatures are small, which implies : (a) that the variation of E_a with T in the intrinsic region is negligible ; (b) that the shift of E_F with temperature is not significant.

In calculating m_e^* and m_h^* it was assumed that these masses are equal (Table 5.2). Following analysis offers a justification for that. In the intrinsic region, assuming an equal number of electrons and holes, i.e $n_i = p_i$, the Fermi energy E_F can be written as [Smith 1968],

$$E_F = \frac{E_g}{2} + \left(\frac{3kT}{4}\right) \ln\left[\frac{m_h^*}{m_e^*}\right] \quad (5.54)$$

where E_g is the width of the forbidden energy gap. Neglecting the variation of E_F with T and assuming that the Fermi level lies midway between the valence and conduction bands, one obtains,

$$(3kT/4)\ln(m_h^*/m_e^*)=0$$

or

$$m_h^* = m_e^*$$

That the effective mass of holes is approximately the same as those of electrons in the intrinsic region is not surprising. At high temperatures, dangling bonds associated with impurities can be ignored, and the material can be considered to be pure; the intrinsic carrier concentration n_i dominates the conductivity. As a result, the Hall coefficient is not expected to vary widely from samples to sample as seen from fig. 5.4. Hence, it can be safely assumed that $n_i = p_i$ at $T \geq T_c$. Furthermore, the constant A in equation (5.52) depends on the effective masses of both types of carrier concentrations.

However, for the same dominant matrix GeO_2 , A is expected to vary little from sample to sample. This is clearly seen from the values of A in Table 5.2. Therefore, with an almost constant value of A and almost equal concentration of electrons and holes in the intrinsic region, one can safely assume that the effective masses of holes and electrons are equal. Taking a representative value of A from Table 5.2 and using equation (5.52) gives

$$m_e^* = m_h^* = 9.22 \times 10^{-29} \text{ kg} = 100m_e$$

Here, m_e is the mass of a free electron. Such a large value of the effective mass is in fact one of the consequences of small polaron theory, where the trapped carrier moves along with the polarisation cloud creating

a large effective mass. For small polaron conduction, an effective mass as high as 9.5×10^{-13} kg has been obtained for Au-SiO_x films in the dielectric regime [Steele et al. 1992]. It may be noted that relatively smaller effective masses have been obtained in non-polaronic conduction in a:Si ($1.1 m_e$), in a: Ge ($0.55 m_e$), and in InSb ($0.18 m_e$) [Putley 1975] corresponding to values of A ($\approx 10^{22}$) which are one hundred times smaller than values observed in Cu-GeO₂ thin films. Higher values of A are also a consequence of the larger activation energies (0.66 to 0.77 eV) found in Cu-GeO₂ films, compared to those of a:Si (0.60 eV), a:Ge (0.392 eV) and InSb (0.125 eV) [Putley 1975].

AC ELECTRICAL CONDUCTIVITY AND DIELECTRIC PROPERTIES

6.1 Introduction

Important information about deep defect states associated with impurities, irregularities and discontinuities of amorphous materials can be obtained from the real part of the frequency dependent conductivity $\sigma_1(\omega)$. This part almost follows a universal law (in the frequency range 10 to 10^6 Hz) viz.,

$$\sigma_1(\omega) \propto \omega^s T^n \quad (6.1)$$

Extensive theoretical [Austin and Mott 1969, Pike 1972, Pollak and Pike 1972, Jonscher 1976, Elliot 1977, 1987, Mott and Davis 1979, Long 1982] and experimental investigations on chalcogenide glasses [Lakatos and Abkowitz 1971, Owen and Robertson 1970, Segawa 1974, Hauser 1983, 1985], and on a:Ge [Narasimhan, Guha, Agarwal 1976] confirm the validity of equation (6.1) with $0 < s \leq 1$ and $n = 0.2$ to 0.4 .

The theoretical models which predict the behaviour in (6.1) can be broadly classified into four groups. Austin-Mott [1969] type quantum-mechanical tunneling (QMT) ascribes the AC loss phenomena to relaxation caused by electron or atomic tunneling between equilibrium sites. In this model the frequency exponent s is predicted to be temperature-independent but frequency-dependent, with s lying in the range $0 < s \leq 1$. Certain experimental observations contradict the predictions of QMT. These are a steady decrease of s from unity with rise in temperature, a very weak temperature-dependence of $\sigma_1(\omega)$ at increasing frequencies, and much lower values of the

density of states $N(E_F)$. The Correlated Barrier Hopping (CBH) model [Pike 1972, Elliot 1977] sought to account for some of the discrepancies observed in QMT. This model, in which two electrons are assumed to hop over a potential barrier between defect sites, predicts a sub-linear frequency dependence of $\sigma_1(\omega)$, yielding values of $N(E_F)$ much lower than those predicted by QMT, and a temperature-dependent s that decreases with increasing temperature. Such features have been observed in a wide variety of amorphous materials, namely As-Te-based glasses [Mott and Davis 1979, Long 1982, Elliot 1977, 1990; Hauser 1983, 1985], transition metal oxide glasses [Sayer and Mansingh 1972, Murawski and Gizowski 1974] and in vanadium dioxide crystals [Mansingh, Sinha, Dheer and Sayer 1984]. The third model, due to Long [1982], is based on quantum-mechanical tunneling of small polarons between states close to the Fermi level. In contrast to Austin-Mott-type QMT and Pike-Elliot CBH, this model predicts a temperature-dependent s which increases to a maximum value of 1.

Most experimental works mentioned in the references above show that for $f > 10^5$ Hz, equation (6.1) is obeyed with s equal to 2. The QMT, CBH and small-polaron tunneling models appear incapable of explaining this phenomenon. Detailed theoretical calculations [Mott et al. 1979] show that this process arises when a phononless, but photon-activated, electronic transition takes place between equilibrium sites. When the photon energy $\hbar\omega$ becomes much greater than thermal energy (kT), the frequency exponent in equation (6.1) will vary as a function of frequency only. In this case, $\sigma_1(\omega)$ will have a quadratic frequency dependence. The next section (6.2) summarizes these four theoretical models with appropriate expressions for AC conductivity, the frequency exponent s , the temperature exponent n and the tunneling distance R_w .

One of the potential sources of difficulties in interpreting AC loss data is the fact that the measured $\sigma(\omega)$ will have a contribution from the DC conductivity. Since $\sigma(\omega)$ for amorphous materials increases monotonically with frequency and is weakly dependent on temperature, the AC component $\sigma_1(\omega)$ will tend to dominate at higher frequencies and lower temperatures. σ_{dc} is usually thermally activated, consequently it will dominate AC conductivity at higher temperatures. Therefore, the total measured conductivity at a given frequency must be decomposed into two parts, namely

$$\sigma(\omega) = \sigma_{dc}(0) + \sigma_1(\omega) \quad (6.2)$$

The validity of equation (6.2) depends mainly on two assumptions [Elliot 1987]. First, AC and DC conductivities should originate from completely separate and different processes, and, secondly, the same basic process may be responsible for both types of conductivity, in which case DC conductivity should not contribute to the overall AC conductivity. The validity of the above two assumptions must be examined for a particular experimental case, before the frequency-dependent behaviour of the AC conductivity is analyzed.

6.2 Origin of frequency dependent conductivity

The fundamental dielectric concepts which provide a framework for some AC conductivity parameters will be discussed in this section and calculated from experimental data. The application of a frequency-dependent electric field $E(\omega)$ to a dielectric material produces a frequency-dependent polarization $P(\omega)$ given by [Jonscher 1976, 1983],

$$P(\omega) = \epsilon_0 \chi(\omega) \omega \quad (6.3)$$

where ε_0 is the permittivity of free space and $\chi(\omega)$ is the complex dielectric susceptibility, given by

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) \quad (6.4)$$

The components of the dielectric susceptibility are related to those of the complex permittivity

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

by

$$\varepsilon'(\omega) = [1 + \chi'(\omega)]\varepsilon_0 \quad (6.5)$$

and

$$\varepsilon''(\omega) = \chi''(\omega)\varepsilon_0 \quad (6.6)$$

For a coplanar geometry of electrodes with a gap d between them, the field distribution may be considered uniform if $t \ll d$, where t is the thickness of the film [Long 1982, Jonscher 1983]. Furthermore, assuming that the dielectric material between the plates is homogeneous and that the electrodes are in firm contact with the material, the complex capacitance $C(\omega)$ of the system can be written as

$$C(\omega) = \varepsilon(\omega)A/d \quad (6.7)$$

or

$$\begin{aligned} C(\omega) &= \varepsilon'(\omega)(A/d) - i\varepsilon''(\omega)(A/d) \\ &= C'(\omega) - iC''(\omega) \end{aligned} \quad (6.8)$$

Here $C'(\omega)$ and $C''(\omega)$ are the real and imaginary components of $C(\omega)$, respectively. A is the area of the plates. The real and imaginary components $\sigma_1(\omega)$ and $\sigma_2(\omega)$, respectively of the AC conductivity can be expressed by,

$$\sigma_1(\omega) = \varepsilon_0\chi'(\omega)\omega = \varepsilon'(\omega)\omega$$

or

$$\varepsilon'(\omega) = \sigma_1(\omega)/\omega \quad (6.9)$$

and

$$\sigma_2(\omega) = \omega \varepsilon''(\omega)$$

or

$$\varepsilon''(\omega) = \sigma_2(\omega) / \omega = C''(\omega) d / A \quad (6.10)$$

The loss tangent is defined as,

$$\tan \delta = C''(\omega) / C'(\omega) = \varepsilon'' / \varepsilon' \quad (6.11)$$

The loss angle δ is the angle by which the phase of the dielectric induction in the material lags behind the driving field $E(\omega)$. If electrodes and sample have a well defined geometry, $\tan \delta$ is not very significant in the interpretation of AC loss data since it represents the ratio of two frequency-dependent parameters. However, if the geometry of the system is unknown or uncertain so that the real and imaginary components of the dielectric permittivity cannot be determined separately, then $\tan \delta$ remains a valuable parameter for the interpretation of AC loss data [Jonscher 1983]. In low-loss materials, where the real part of the permittivity ($\varepsilon'(\omega)$) almost remains constant, frequency dependence of $\tan \delta$ is the same as that of $\varepsilon''(\omega)$.

6.3 Mechanisms of polarization

Depending on the frequency spectrum of the investigation, several mechanisms of polarization exist in amorphous materials, each of which contribute to the dielectric parameters in different regions of the frequency spectrum. In the frequency range of the present work (i.e. 10^4 to 10^6 Hz), the two most important mechanisms are Debye dipolar polarization and polarization by hopping charge carriers. Following Jonscher [1976] and Elliot [1987], a brief account of Debye dipolar mechanism is given below. The second mechanism i.e.

polarization by hopping carriers will be discussed with the Pike-Elliott CBH model in section (6.4.5).

6.3.1 The Debye dipolar polarization

In the context of this polarization process in non-crystalline materials, the dielectric response of a pair of localized sites to an applied alternating electric field $E(\omega)$ is considered. The Debye response is defined by the relaxation of the polarization P (eqn. 6.3) on removal of $E(\omega)$. The exciting field changes the relative orientation of a pair of centres and causes transitions between them governed by the intrinsic relaxation time τ of the pair. The dynamic response of the system is then given by [Jonscher 1976],

$$\chi(\omega) \propto \frac{1-i\omega\tau}{1+\omega^2\tau^2} \quad (6.12)$$

By equating real and imaginary parts of $\chi(\omega)$ from equations (6.4) and (6.12), one obtains,

$$\chi'(\omega) \approx \frac{1}{1+\omega^2\tau^2} \quad (6.13)$$

and

$$\chi''(\omega) \approx \frac{\omega\tau}{1+\omega^2\tau^2} \quad (6.14)$$

Equation (6.14) predicts that the dielectric loss $\chi''(\omega)$ will have a peak at $\tau=1/\omega$ if the relaxation time τ has a constant value. However, in non-crystalline materials, the random distribution of localized sites arising out of the disordered structure of the materials ensures that a broad distribution of relaxation times, $n(\tau)$, will exist. Therefore, a peak, not necessarily Debye-like, may appear in the dielectric loss. In this case, the AC conductivity $\sigma_1(\omega)$ will be given by the summation of all microscopic contributions. For a continuous distribution of $n(\tau)$,

the AC conductivity can be obtained from equations (6.9) and (6.14) i.e.

$$\sigma_1(\omega) = \int_0^\infty \epsilon_0 \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} d\tau n(\tau) \alpha \quad (6.15)$$

where α is the polarisability of a pair of sites. If $n(\tau) \propto 1/\tau$, as assumed in many amorphous materials, then equation (6.15) can be written as

$$\sigma_1(\omega) \propto \int_0^\infty \epsilon_0 \frac{\omega}{1 + \omega^2 \tau^2} d(\omega \tau) \propto \omega^s \quad (6.16)$$

where s is the frequency exponent having values in the range $0 < s \leq 1$. Equation (6.16) provides the foundation for the universal behaviour embedded in equation (6.1).

A broad distribution of relaxation times leading to non-Debye-like temperature-and frequency-dependent relaxation peaks implies that the relaxation time itself may be a function of barrier height (W) and intersite separation (R) or a combination of both. Thus, for classical hopping of carriers over the barrier height

$$\tau = \tau_0 e^{W/kT} \quad (6.17)$$

For phonon-assisted quantum mechanical tunneling through the barrier separating two equilibrium sites,

$$\tau = \tau_0 e^{2\alpha R} \quad (6.18)$$

For low frequency and high temperature losses, the probability of transition may involve a combination of the above two expressions [Mott et al. 1979, Long et al. 1982), i.e.

$$\tau = \tau_0 e^{W/kT} e^{2\alpha R} \quad (6.19)$$

Here τ_0 is the constant characteristic relaxation time for lattice distortion.

6.4 Models for AC loss by relaxation processes in amorphous semiconductors

The microscopic relaxation processes leading to equations (6.15) and (6.16) form the basis of a wide variety of AC conduction models in amorphous semiconductors. As to which form of τ in equations (6.17-6.19) should be used in AC-loss calculations depends on the particular type of microscopic relaxation processes observed experimentally. Relaxation may be either due to phonon assisted quantum mechanical tunneling or due to carrier hopping over potential barrier.

Relaxation due to quantum-mechanical tunneling, a process which involves direct coupling due to overlap of the exponentially decaying wave functions of two sites, involves the following processes:

- a) Electron tunneling;
- b) Small polaron tunneling;
- c) Large polaron tunneling;
- d) Atomic tunneling

The process involving thermal-activation of the relaxation time (eqn. 6.17) is due to hopping of carriers over the potential barrier between two sites. This largely involves the following two mechanisms,

- a) Atomic hopping
- b) Correlated Barrier Hopping (CBH)

At high frequency (see section (1.4.3)) relaxations due to QMT and/or carrier hopping appear incapable of accounting for AC loss data. The resonant process, which

does not involve relaxation of any kind, but instead arises from the resonant absorption of a photon, satisfies many features of high frequency AC loss behaviour [Mott et al. 1979].

The essential features of all these models are summarized below except for atomic tunneling and atomic hopping. These two models predict a linear frequency-dependent AC loss (i.e. $s=1$) and a frequency-independent hopping distance, both of which are found to be at variance with the experimental AC loss behaviour in Cu-GeO₂ thin films. Hence these two models will not be discussed further.

6.4.1 Electron tunneling

This model predicts that AC conduction occurs by thermally-assisted QMT between localized states lying very close to Fermi level. This theory was first formulated by Pollak et al. [1961] to explain the AC loss results in doped crystalline Si in which $\sigma_1(\omega) \propto \omega^s$ with s equal to 0.8. Later, Austin et al. [1969] modified the theory to describe the conduction processes through localized states lying close to the Fermi level in amorphous semiconductors. In their model, the relaxation time is given by equation (6.18). Assuming that the defect states are randomly distributed in space and energy, Austin et al. [1969] derived the real part of the AC conductivity as

$$\sigma_1(\omega) = \frac{Ce^2kT}{\alpha} N^2(E_F) \omega R_\omega^4 \quad (6.20)$$

Here, $N(E_F)$ is the density of states at the Fermi level, $C=\pi^2/12$ and R_ω is the tunneling distance given by,

$$R_\omega = \frac{1}{2\alpha} \ln\left(\frac{1}{\omega\tau_0}\right) \quad (6.21)$$

where τ_0 is the characteristic constant relaxation time of the order of an optical phonon frequency, viz. 10^{-13} s. Equation (6.21) predicts that the tunneling distance is a function of frequency alone, is independent of temperature, -a feature contradicted by many experimental observations in chalcogenide glasses, a:Si and oxide glasses. Furthermore, assuming $\sigma_1(\omega) \propto \omega^s T^n$, Long [1982] and Elliot [1987] derived s as

$$s = 1 + \frac{4}{\ln(\omega\tau_0)} \quad (6.22)$$

Assuming $\tau_0 = 10^{-13}$ s and $\omega = 10^4$ s⁻¹ equation (6.22) correctly predicts the values of s (=0.8) as observed by Pollak et al. [1961] in doped crystalline Si. However, equation (6.22) also predicts that s is temperature-independent and decreases with increasing frequency. This feature of the electron tunneling model is in sharp contrast to the experimental observations as mentioned before (see sections (1.4.1) and (1.4.2)). Furthermore, $N(E_F)$, calculated on the basis of equation (6.20) gives relatively higher values (10^{18} to 10^{20} eV⁻¹ cm⁻³) than those obtained from optical absorption studies [Elliot 1987]. Because of these differences, an alternative model was developed within the context of QMT which accurately describe the behaviour of s and other AC loss data. This model is described in the next section.

6.4.2 Small polaron tunneling model

It may be recalled (sections (4.4.2), (4.4.3) and (5.7.1)) that DC conductivity in Cu-GeO₂ films is best described by the small polaron model below the critical temperature T_C . One might hope, therefore, that the same mechanism may be operative in AC conductivity. Small polarons are assumed to be highly localized so that their distortion clouds do not overlap and, consequently, their activation energy (W) is independent of the site-separation. The

relaxation time for small polaron tunneling, in the limit of non-adiabatic approximation, at high temperatures, is given by equation (6.19) which is temperature-dependent. This in turn leads to a temperature-dependent tunneling distance R_ω [Long 1982, Elliot 1987],

$$R_\omega = -\frac{1}{2\alpha} [\ln(\omega\tau_{ot}) + \frac{W}{kT}] \quad (6.23)$$

where τ_{ot} is the constant characteristic relaxation time for small polaron tunneling. The AC conductivity is still given by equation (6.20) but R_ω is replaced by equation (6.23). Equation (6.23) predicts that R_ω decreases more rapidly with increasing frequency than is predicted by equation (6.21). Theoretically, R_ω and hence $\sigma_1(\omega)$ will fall rapidly to zero at a cut-off frequency f_m given by ,

$$f_m = \frac{1}{\tau_{ot}} e^{-W/kT} \quad (6.24)$$

Now assuming $\sigma_1(\omega) \propto \omega^s$, the frequency exponent s can be defined as,

$$s = \frac{d[\ln \sigma(\omega)]}{d[\ln \omega]} \quad (6.25)$$

Substituting equation (6.20) into equation (6.25) with R_ω replaced by equation (6.23), Long [1982] and Elliot [1987] derived s as

$$s = 1 + \frac{4}{[\ln(\omega\tau_{ot}) + W/kT]} \quad (6.26)$$

This equation predicts an exponent s which increases with temperature within the range $0 < s \leq 1$. The temperature exponent n is given by [Long 1982],

$$n = 1 - \frac{4}{1 + (kT/W) \ln(\omega\tau_{ot})} \quad (6.27)$$

Equations (6.23), (6.24) and (6.26) predict that s can take negative values as the frequency is increased towards f_m at which both R_ω and $\sigma_1(\omega)$ will have minimum values. However, as Elliot [1987] pointed out, physically R_ω cannot be less than the inter-atomic distance. Therefore, for frequency greater than the cut-off frequency, the small polaron contribution to the overall AC conductivity will be negligible. It will be seen later that these features conform to the AC loss data observed in Cu-GeO₂ thin films, in the sense that below the cut-off frequency $f_m (\leq 10^5 \text{ Hz})$, small polaron tunneling dominates the conduction while above f_m conduction is dominated by a photon-activated resonant process.

6.4.3 Large polaron tunneling model

The small polaron tunneling model predicts that s increases with temperature and decreases with frequency. In contrast to these predictions, there is an evidence that in binary V₂O₅-P₂O₅ glasses [Murawski 1984] and in sputtered Germanium [Long 1982], s decreases from unity with increasing temperature, and may exhibit a minimum at a certain temperature before increasing again in a similar fashion to the small polaron model. Long's [1982] large polaron model appears to account for this kind of behaviour. The underlying mechanism is still the QMT process but where an overlap of potential wells of two sites occurs. The resultant excitation is a polaron which has a long range of coulombic interaction extending over many interatomic distances. For such polarons, the hopping energy W is reduced because of the overlapping wells and is given by [Austin et al. 1969],

$$W = (e^2 / 4\epsilon_p) \left(\frac{1}{r_p} - \frac{1}{R} \right) = W_0 \left(1 - \frac{r_p}{R} \right) \quad (6.28)$$

where r_p is the polaron radius, R is the tunneling distance, W_0 is the hopping energy for non-overlapping potential wells, and ε_p is given by,

$$\varepsilon_p \approx \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \quad (6.29)$$

Here, ε_s and ε_∞ are the static and high frequency dielectric constants of the material respectively. Because of the reduction in W at smaller values of R , the relaxation time is still given by (6.19) but with W given by equation (6.28). On substituting equations (6.19) and (6.28) into equation (6.15), Long [1982] derived the following expression for AC conductivity,

$$\sigma_1(\omega) = (\pi/12)e^2(kT)^2 N^2(E_F) \left(\frac{\omega R_\omega^4}{2\alpha kT + W_0 R_p / R_\omega^2} \right) \quad (6.30)$$

The frequency exponent s may now be found by substituting equation (6.30) into equation (6.25), i.e.

$$s = 1 - (1/R_\omega') \left[\frac{4 + 6W_0 r_p' / kTR_\omega'^2}{(1 + W_0 r_p' / kTR_\omega'^2)^2} \right] \quad (6.31)$$

Here $R\omega' = 2\alpha R_\omega$ and $r_p' = 2\alpha r_p$.

Equation (6.31) suggests that s is both a temperature and a frequency-dependent parameter, and that it decreases from unity with increasing temperature. For small values of r_p' , s exhibits a minimum at,

$$s_{\min} = 1 - 5/2 \left(\frac{W_0 r_p'}{kT} \right)^{1/2} \quad (6.32)$$

before increasing again in a similar way to small polaron QMT.

6.4.4 The resonant process

The AC conductivity in Cu-GeO₂ films shows an almost $s=2$ behaviour at higher frequency range 10^5 - 10^6 Hz. A relaxation process involving photon-assisted tunneling or hopping appears incapable of accounting for this. Mott et al. [1979] contend that such a quadratic behaviour of AC conductivity arises from the resonant absorption of a photon (associated with applied electric field $E(\omega)$) by sites whose ground state energy level has been split (due to spin-orbit interactions) by ΔE . The resonant absorption of a photon occurs when photon energy $\hbar\omega = \Delta E$. As a result, a phononless but photon-activated electronic transition can take place between two sites. The random orientation of localized sites in a disordered system ensures that photon absorption will occur over a wide range of frequencies.

Mott and Davis [1979] considered the contributions of this process to the AC loss of amorphous semiconductors in the high photon energy limit i.e. $\hbar\omega \gg kT$. Considering two localized sites at separation R , the ground state splitting of the energy level by resonance interaction is given by,

$$\begin{aligned}\Delta E &= 2I_0 e^{-\alpha R} \\ &= 2I\end{aligned}\tag{6.33}$$

where I is the overlap integral between two sites given by $I = I_0 e^{-\alpha R}$ and α is the localization length of the states, defined in a manner which interprets $e^{-\alpha R}$ as the rate at which wave functions on the sites fall with distance. From equation (6.33) we see that photon-assisted transition will occur when two sites are separated by the distance R given by,

$$R = (1/\alpha) \ln(2I_0 / \hbar\omega)\tag{6.34}$$

Mott and Davis [1979] developed a conductivity expression for this process as

$$\sigma_1 = (Ce^2 / \alpha) [N(E_F)]^2 \omega^2 R^4 \quad (6.35)$$

with $C = \pi^2 / 2$. Substituting equation (6.35) into equation (6.25), allows the frequency exponent s to be calculated as [Elliot 1987]

$$s = 2 - \frac{4}{\ln(2I_0 / \hbar\omega)} \quad (6.36)$$

This expression suggests that the AC conductivity essentially follows a quadratic behaviour; a slight deviation from $s=2$ occurs due to the weakly-varying logarithmic term in the denominator of (6.36).

6.4.5 Relaxation due to hopping: The Pike-Elliot CBH model

In this mechanism thermally-activated charge carriers are assumed to hop over a potential barrier between two defect sites, in contrast to QMT of the carriers through the barriers. It predicts a sublinear frequency dependence of AC conductivity, yielding values of $N(E_F)$ much lower than those predicted by QMT, and a temperature-dependent s that increases towards unity as the temperature is lowered towards absolute zero. Basically there are two kinds of hopping models which are invoked to explain AC loss data in semiconductor materials. The first one, initially developed by Pollak and Pike [1972], is called the atomic hopping model in which ionized atoms are assumed to hop over the potential barrier of height W separating the two defect sites. The relaxation time in this process is given by equation (6.17), which is independent of the intersite separation R . As a consequence, the hopping distance becomes

independent of frequency yielding a $\sigma_1(\omega)$ which is linearly-dependent on frequency and temperature. These predictions have been found to be at variance with experimental results of Cu-GeO₂ thin films and, therefore, will not be discussed further.

Because of difficulties with relaxation processes associated with QMT, an alternative model, which correlates the potential barrier height (W) with intersite separation R , was proposed by Pike [1972] for single electron hopping. It was later extended by Elliot [1977] for simultaneous two-electron hopping. In this model, each site is assumed to have a coulombic potential associated with it. For neighbouring sites separated by a distance R , the coulomb wells overlap, resulting in a lowering of the effective barrier height from W_M to a value W (see fig. 6.1). W_M is the value of the maximum barrier height at infinite intersite separation i.e. the energy required to remove one electron from localized site into an extended state. The relationship between W and W_M is given by Elliot [1977] as

$$W = W_M - \frac{4ne^2}{KR} \quad (6.37)$$

Here K is the effective dielectric constant of the material and n is the number of electrons that hop. In the case of two-electron hopping, equation (6.37) becomes,

$$W = W_M - \frac{8e^2}{KR} = W_M - \frac{8e^2}{4\pi\epsilon\epsilon_0 R} \quad (6.38)$$

For hopping over the barrier, the relaxation time is given by equation (6.17) with W given by equation (6.37) i.e.,

$$\tau = \tau_0 e^{[-(W_M - 8e^2/KR)/kT]} \quad (6.39)$$

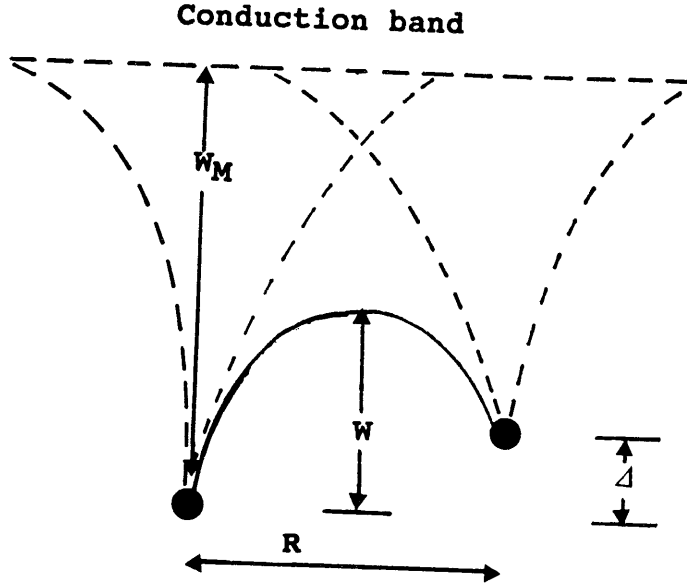


Fig.6.1 Schematic representation of the lowering of the barrier height for two charged sites in the CBH model [Elliot 1977, 1987]. W is the height of the barrier over which the carriers must hop. Δ is the disorder energy.

In the narrow band limit i.e. $\Delta \ll kT$, where Δ is the disorder energy, and assuming that the centres are distributed randomly in space, the AC conductivity, calculated using equation (6.15), [Pike 1972, Elliot 1977, Long 1982] becomes

$$\sigma_1(\omega) = (2/24)\pi^3 N^2 \epsilon_0 \epsilon \omega R_\omega^6 \quad (6.40)$$

where the hopping distance at a frequency ω is given by,

$$R_\omega = \frac{2e^2}{\pi \epsilon \epsilon_0 [W_M + kT \ln(\omega \tau_0)]} \quad (6.41)$$

Substituting equation (6.40) into equation (6.25) gives s as [Long 1982],

$$s = 1 - \frac{6kT}{W_M + kT \ln(\omega\tau_0)} \quad (6.42)$$

The temperature exponent n , in the narrow band limit, also calculated by Long [1982], is found to be

$$n = -(1-s) \ln(\omega\tau_0) \quad (6.43)$$

Equation (6.41) indicates that, in contrast to QMT models, the hopping distance will vary with both temperature and frequency, and it is this coupling which is reflected in equations (6.42) and (6.43).

The CBH model was found to describe the AC loss behaviour accurately in a wide variety of chalcogenide and oxide glasses. A critical test of the model comes from the temperature-dependence of conductivity and its frequency exponent. Equation (6.42) predicts s to increase with increasing frequency and decrease with increasing temperature for small values of W_M/kT , in contrast to QMT-models predictions. For large values of W_M/kT , s lies close to unity. The model correctly predicts the AC loss behaviour with a narrow distribution of relaxation times $\tau \approx 10^{-13}$ to 10^{-12} s in a wide variety of semiconducting materials. The model also predicts realistic values of the density of states ($\approx 10^{19}$ eV⁻¹ cm⁻³) in contrast to unreasonably high values ($\approx 10^{21}$ eV⁻¹ cm⁻³) predicted by QMT models.

6.5 Experimental procedure

6.5.1 Film preparation

410 nm thick 30 at.wt.% Cu-70 at.wt.% GeO₂ films were deposited on ultrasonically cleaned 7059 glass substrates

by electron beam evaporation from a single graphite boat at a pressure $\approx 10^{-3}$ to 10^{-4} Pa. The technique has been described in sections (3.4.1) and (4.3.1).

6.5.2 Conductance and capacitance measurements

Aluminum electrodes of dimensions 4.5 mm x 2 mm with a gap of 1.5 mm between them were thermally-evaporated onto the films to produce a coplanar geometry. The main advantage of using a coplanar geometry is that the sheet resistance is very high, about 10^{10} ohms at room temperature. This masks any contact effects and the substrate contribution to the AC loss becomes very small [Narsimhan et al. 1976, Agarwal et al. 1975, Long et al. 1982]. Since the film thickness t (410 nm) is much less than the electrode separation d (1.5 mm), the field distribution in the gap may be assumed uniform. The deposition conditions, composition of the samples and the thicknesses were identical to those of DC conductivity, Hall effect and optical studies in order to allow ready comparison of the results.

All electrical measurements were taken inside a DN 1714 (Oxford Instrument) variable temperature liquid nitrogen cryostat at a pressure $\approx 10^{-2}$ Pa. Normally, the upper temperature limit of the cryostat is 300 K. This range was extended to 500 K by fitting a high temperature sapphire window to the sample space. The sample was first attached to the holder with silicone compound, and then two connecting leads were pressed on to the electrodes with silver epoxy paste. The sample holder was then loaded into the sample space. The electrical connections to the heater (ITC4 Oxford Instrument) and the temperature sensor were established via a 10-pin electrical feed through on top of the sample holder [see plate 5].

The temperature of the samples was varied in the range 150 to 425 K (within an uncertainty of 2 to 3 %) using a ITC4 temperature controller. The conductance (G), capacitance (C), loss tangent (D) and quality factor (Q) were all measured in the frequency range 10^4 to 10^6 Hz using a HP 4275A LCZ meter in the two-terminal configuration. A schematic diagram of the measurement circuit is shown in fig. 6.2.

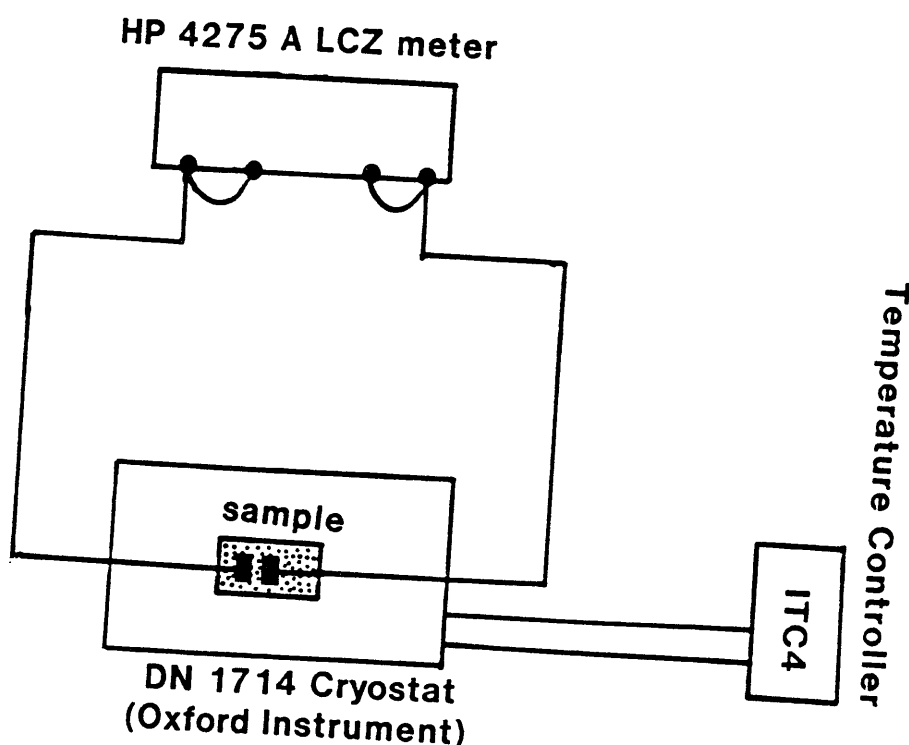


Fig.6.2: Schematic representation of AC conductivity measurement system.

Measurements were made in the parallel-mode as shown in fig. 6.3a. This circuit mode was chosen because of the sample's very low capacitance and high impedance. However, the actual equivalent circuit of the sample was identified from the results of trial measurements. The trial results show that the dissipation factor (D) increases in the higher frequency range (10^5 to 10^6 Hz).

It will be shown in section (6.6.1) that this increase is consistent if the three element parallel circuit (fig. 6.3a) is first converted to an effective parallel circuit (fig. 6.3b) and, then to a two-element equivalent series circuit shown in fig. 6.3c.

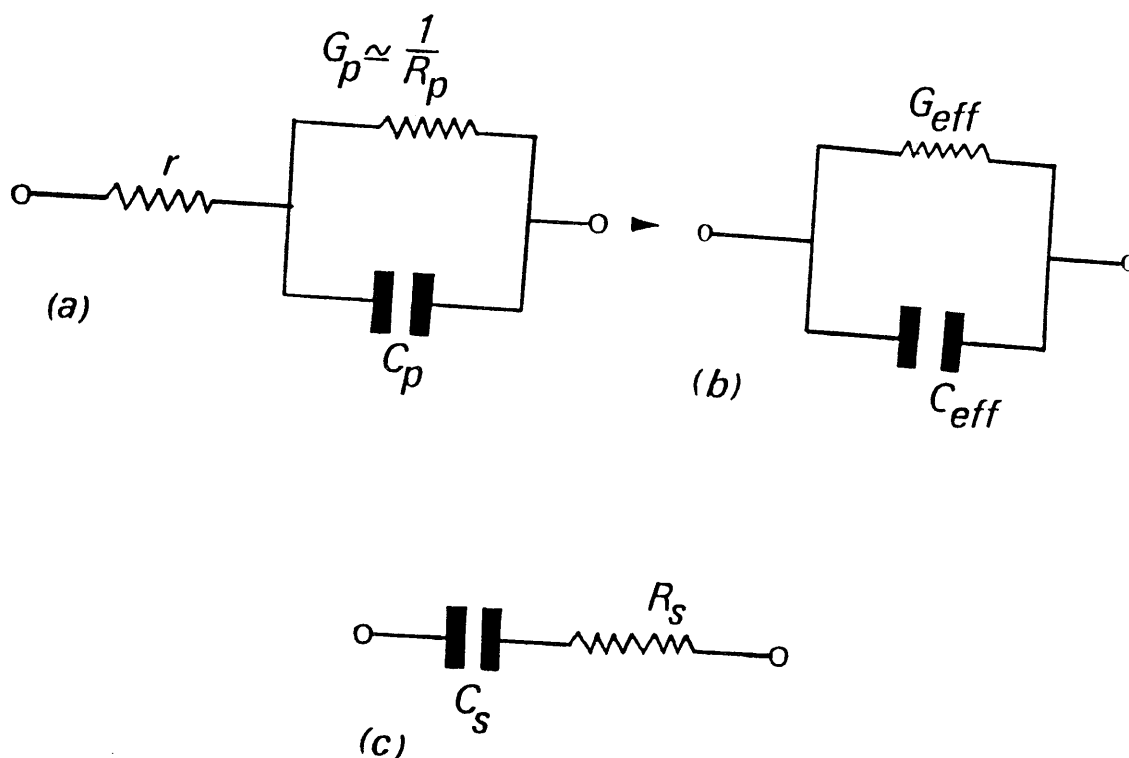


Fig.6.3: (a) Three element circuit mode at any given temperature and frequency; (b) Effective parallel circuit mode; (c) Two element equivalent series circuit mode.

6.5.3 Order of accuracy, uncertainty and reproducibility of the measurements

The measuring range of the HP 4275 A LCZ meter is from 0.01 fF to 199.99 μ F for C, 0.00001 to 9.9999 for D, 0.01 to 9000 for Q, 0.01 nS to 19.999 S for G and 0.01 m Ω to 19.999 M Ω for impedance. All these parameters were measured with a basic accuracy of ± 0.1 to 5%. The high resolution operating mode provides 5 1/2 digit resolution

for all parameters. A total of 10 test signal-frequencies, which have accuracy of $\pm 0.01\%$ were available in the range 10 kHz to 1 MHz. The test signal was sinusoidal and could be set at the desired amplitude in the range from 1 mV to 1 V r.m.s. For the present measurements, a 0.8 V r.m.s was applied across the electrodes.

The HP LCZ meter employs certain unique functions which make it possible to eliminate background effects effectively. A digital offset adjustment function measures residual capacitance, inductance and resistance inherent to connecting leads and test fixtures, and offsets these parasitic impedances to zero with respect to the measured values. Any measurement error due to these effects was, therefore, automatically eliminated for stray capacitance up to 20 pF, residual inductance up to 2000 nH, resistance up to 0.5 ohms and conductance up to $5\mu\text{S}$. Within the lower frequency range (10 kHz to 40 kHz) there was a 10 to 20% uncertainty in the values of C, G and D whereas in the higher frequency range all readings were stable. Thus, readings were first taken in ascending order of frequency and later the steps were repeated in descending order. No significant differences were observed in the two sets of readings. Consequently, only the ascending-order readings were taken.

The samples were left overnight and the reproducibility of the measurements were checked the following morning. Again no significant dispersion of the measurements were observed.

6.5.4 Experimental precautions

Stray capacitance existing around component leads and contact electrodes contribute significantly to measurement errors in high impedance materials. To reduce

such effects, connecting leads were kept as short as possible and the contacts to electrodes were made with low resistivity silver epoxy paste. To minimize the effects of surface leakage currents, a guard ring was introduced by connecting the terminal of the sample to the ground terminal of the HP LCZ meter.

Conductance and capacitance offset adjustments were performed by connecting test leads to the unknown terminals (i.e. not to the sample) and by activating the zero-offset button. Next, inductance and resistance offset adjustments were automatically performed by short-circuiting the unknown terminals. Having performed these two offset measurements, test leads were then connected to the sample electrodes. The measured values of the residual capacitance (0.0002 pF) and resistance (5Ω) were automatically displayed.

An important and significant source of error is the effect of test leads on the AC loss parameters. The propagation signal in the connecting leads will develop a change in phase between two points: the difference in phase corresponds to the ratio of the distance between two points to the wavelength of the propagating signal. As a result, test leads cause a phase shift and a propagation-loss of the test signal.

For high resistivity materials, the effect of cable length becomes acute at frequencies $>10^6$ Hz. To minimize this effect, all measurements in this experiment were taken at and below 10^6 Hz. Furthermore, the 1 m cable length-switch on HP 4275A front panel was selected for bringing the measuring bridge circuit to its optimum balance and for minimizing the measurement errors when cables of length 1 m, or greater, was used. Since the characteristic impedance of the test cable is also a

contributing factor in the propagation-loss and phase shift, use of different types of test cables was avoided.

6.6 Results and discussions

6.6.1 Variation of capacitance, loss tangent and dielectric loss with frequency and temperature

Figs. 6.4 and 6.5 show the variation of capacitance with frequency at different temperatures and the variation with temperature at different frequencies. The magnitude of the capacitance at a given temperature and frequency lies in the range 1.13×10^{-13} F to 1.25×10^{-13} F. It decreases slightly as frequency is increased to 10^5 Hz. The decrease is more prominent at lower frequencies and higher temperatures. At higher frequencies ($f > 10^5$ Hz) and lower temperatures ($T \leq 250$ K), the capacitance shows very little dependence on frequency. Fig. 6.5 indicates that the capacitance increases as temperature is increased at all frequencies. Throughout the entire temperature range 150 to 425 K, capacitance shows a weak frequency-dependence. All curves saturate to a constant value at around 150K.

The variation of loss tangent ($\tan \delta$) with frequency is shown in fig. 6.6: it consists of two frequency regions. In the lower frequency region (10^4 to 10^5 Hz), the loss factor decreases sharply, showing two loss minima over a relatively narrow range, $f_m : 10^5$ to 2×10^5 Hz. Beyond these, $\tan \delta$ increases rapidly but no sign of a maximum. Values of f_m and $\tan \delta$ shift towards slightly higher values with increase in temperature .

The real part of the dielectric constant (ϵ' / ϵ_0) was calculated from the geometry of the sample using equation (6.7). The values ($\approx 10^4$) showed little variation with temperature and frequency. Some typical

values of (ϵ'/ϵ_0) at 150 K are listed in Table 6.2. The dielectric constant (ϵ'/ϵ_0) , also known as dielectric loss, was calculated from the values of ϵ'/ϵ_0 and $\tan\delta$ using equation (6.11). This parameter shows negligible variation with temperature but varies widely with frequency. Some typical values at 150 K are listed in Table 6.2. Values of dielectric constant running into thousands have been reported for a vast number of oxide dielectric materials such as Al_2O_3 , Ta_2O_5 and MnO_2 [Harrop 1972, Tareev 1975, Jonscher 1983]. This further confirms the IR and X-ray results that Cu- GeO_2 matrix is dominated by the oxide component GeO_2 (see sections (3.4.1) and (3.4.3)).

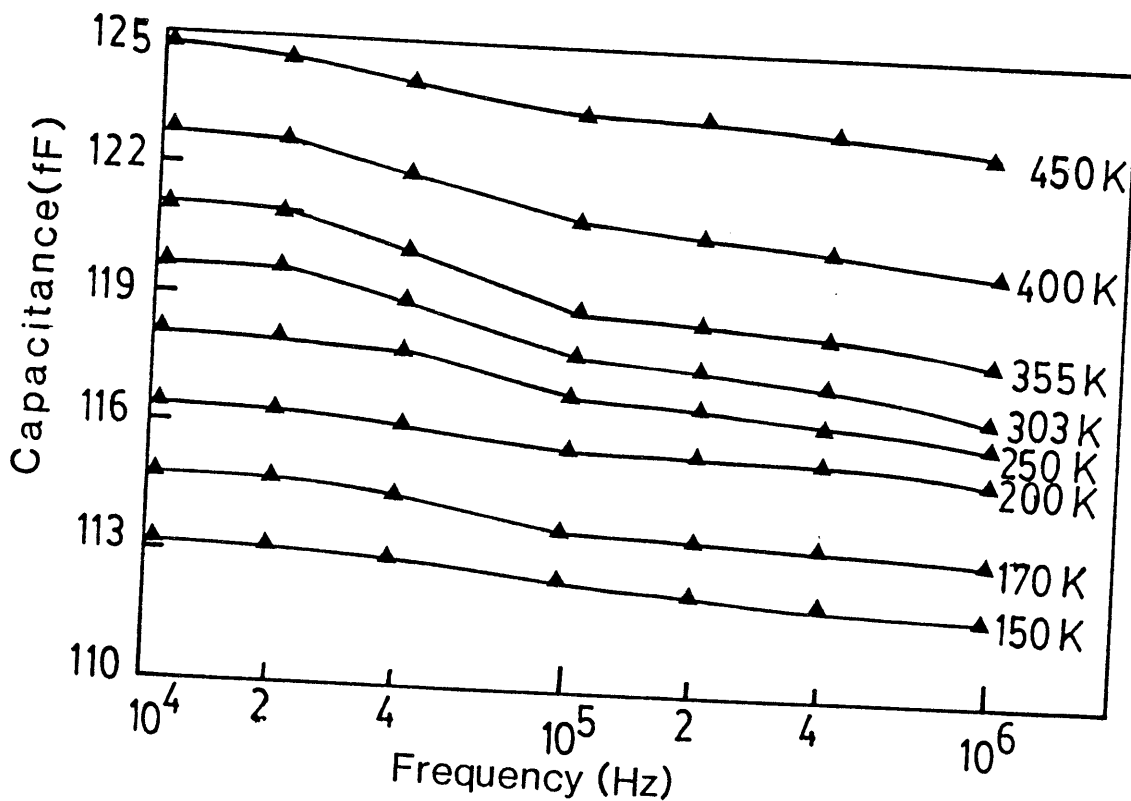


Fig.6.4: Variation of capacitance with frequency at different temperatures.

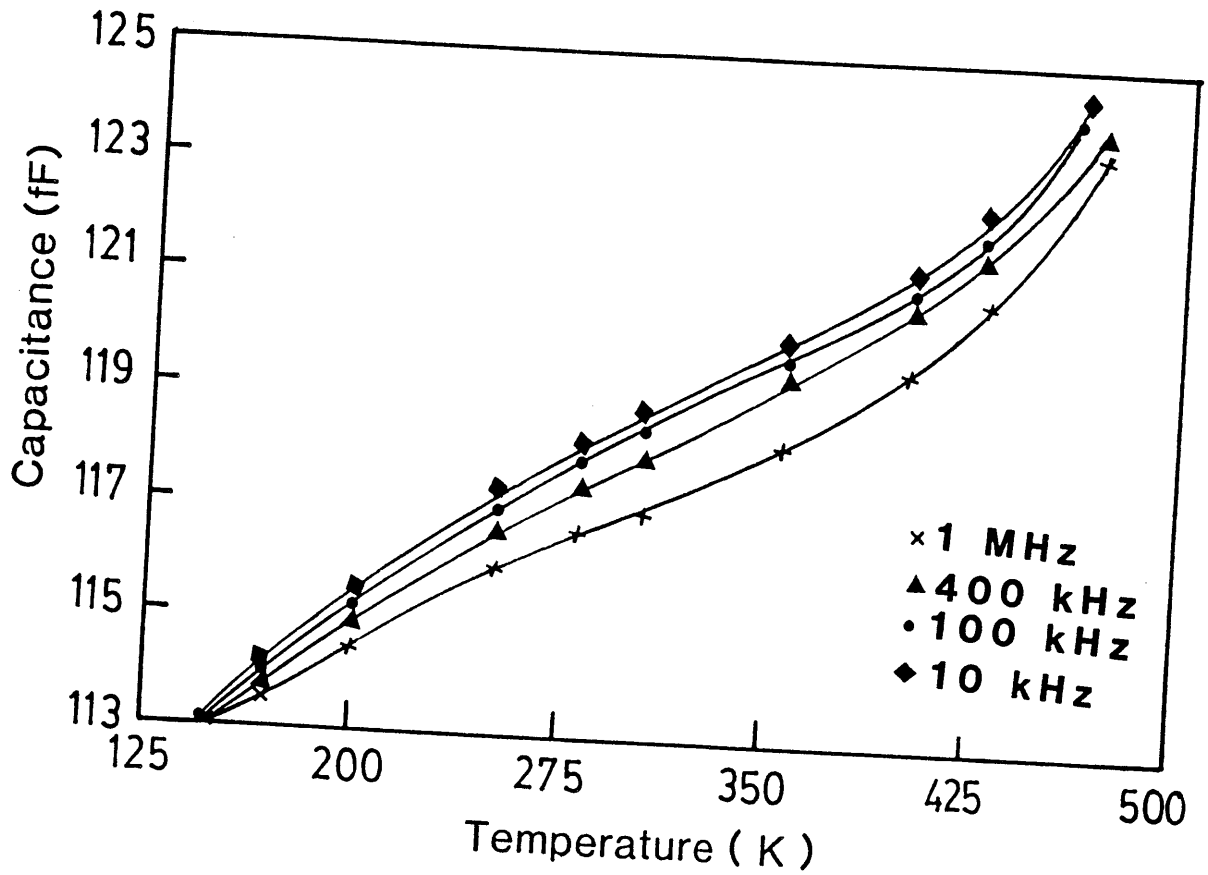


Fig.6.5: Variation of capacitance with temperature at different frequencies.

However, the large relative permittivity of Cu-GeO₂ cermet system observed in the present work may also indicate that, in planar geometry, the dielectric response was partially governed by the substrate. This was tested by measuring the response of a bare substrate with electrodes. It was found that the substrate contributions to C, G and D were about 30%. It is uncertain, however, to what extent this affects the actual measurements on a cermet-glass substrate composite system. Furthermore, no minimum was observed in the

spectral behaviour of G and D. It has been argued [Narsimhan et al. 1976, Agarwal et al. 1975, Long et al. 1982] that if the film thickness(t) is much smaller than the thickness of the glass substrate, then the electric field-penetration into the substrate may be negligible. Since in the present work the film thickness t (410 nm) is much less than the substrate-thickness (2 mm), it is assumed that the observed temperature or frequency dependence of the dielectric response is largely due to the film.

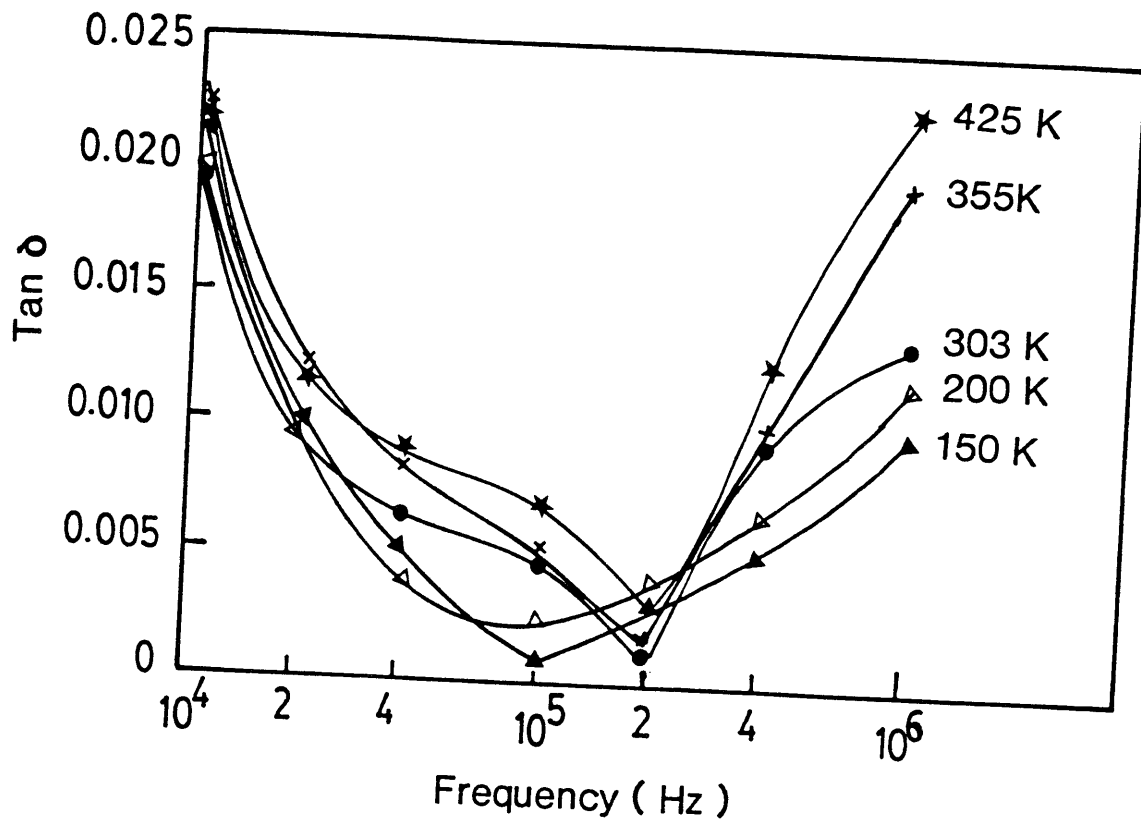


Fig.6.6: Variation of loss tangent with frequency at different temperatures.

Fig. 6.7 shows the variation of the dielectric loss with frequency. Now the real part of the conductivity $\sigma_1(\omega)$ is expressed in terms of the dielectric loss by equation (6.9). Substituting $\sigma_1(\omega)$ from equation (6.1) into equation (6.9), one obtains,

$$\varepsilon''(\omega) \approx \omega^{s-1} T^n \quad (6.44)$$

Table 6.1 shows the values of s estimated from the slope $(s-1)$ of fig.6.7 as a function of temperature for the two frequency regions.

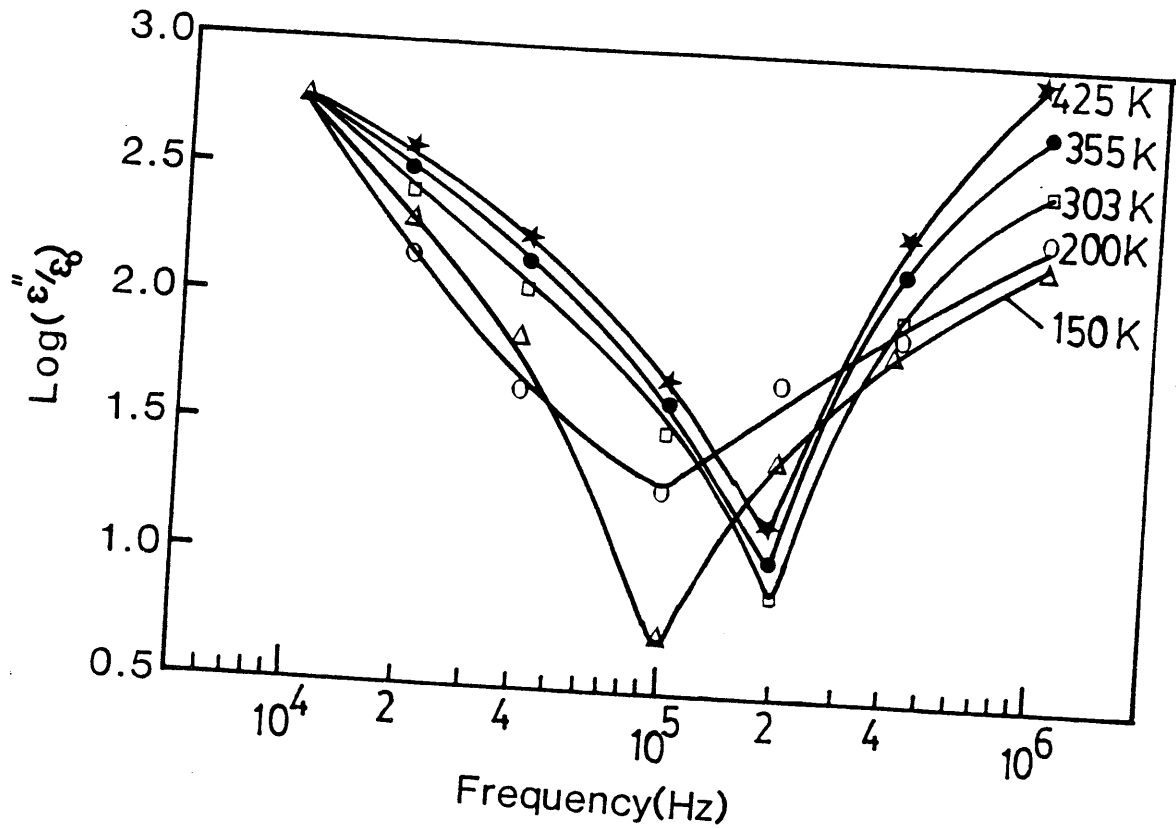


Fig.6.7: Frequency dependence of dielectric loss ($\varepsilon''/\varepsilon_0$) at different temperatures.

The dielectric loss curves in fig. 6.7 show a similar frequency-dependence as that of $\text{Tan}\delta$ in fig. 6.6, although absolute values are different. This kind of behaviour suggests, in view of equation (6.11), that dispersion of ϵ' is negligible, which is indicative of a low-loss material [Jonscher 1983]. Some of these features are in conformity with those observed in thin films of ZnS [Goswami et al. 1973], Copper phthalocyanine [Gould and Hassan 1983] and SiO/SnO_2 [Rahman et al. 1987]. A qualitative analysis of the situation may be presented in the following way.

At a given frequency the circuits in figs. 6.3b and 6.3c have equal impedance, i.e. $Z_{\text{eff}} = Z_s$, where

$$Z_{\text{eff}} = r + \frac{R_p}{1 + j\omega C_p R_p} \quad (6.45)$$

and

$$Z_s = R_s + \frac{1}{j\omega C_s} \quad (6.46)$$

Here, C_s and R_s are the equivalent series capacitance and resistance, and C_p and R_p are the parallel mode capacitance and resistance respectively. Z_{eff} is the effective impedance of the circuit in fig. 6.3b. Equating the real and imaginary parts of these two equations, one obtains,

$$C_s = \frac{1 + \omega^2 R_p^2 C_p^2}{\omega^2 R_p^2 C_p^2} = (1 + D^2) C_p \quad (6.47)$$

where D , the diffusion (or loss) factor, is equal to $1/\omega R_p C_p$ and

$$R_s = r + \left(\frac{D^2}{1 + D^2} \right) R_p \quad (6.48)$$

Taking $\text{Tan}\delta = \omega R_s C_s$ in the equivalent circuit of fig. 6.3c, Goswami et al. (1973) and Tareev (1975) derived,

$$\text{Tan}\delta = \omega R_p C_p = D(1+r/R_p) + \omega r C_p \quad (6.49)$$

Substituting the value of D into equation (6.49), one obtains in the limit $r/R_p \ll 1$,

$$\text{Tan}\delta = \frac{1}{\omega R_p C_p} + \omega r C_p \quad (6.50)$$

First and second derivative of equation (6.49) can be written as (assuming that C_p is not affected by frequency)

$$\text{Tan}'\delta = \left[-\frac{1}{\omega^2 R_p C_p} (1+r/R_p) + C_p r \right] \quad (6.51)$$

and

$$\text{Tan}''\delta = \frac{2}{\omega^3 R_p C_p} (1+r/R_p) \quad (6.52)$$

Equation (6.52) is positive for all values of ω , R_p , C_p and r . This suggests that $\text{Tan}\delta$ possesses a minimum at a cut-off frequency given by $\text{Tan}'\delta = 0$. In the limit $r \ll R_p$ equation (6.51) yields,

$$\omega_{\min} = \left(\frac{1}{r R_p C_p^2} \right)^{1/2} \quad (6.53)$$

The frequency dependence of $\text{Tan}\delta$ (fig.6.6) and dielectric loss (ϵ''/ϵ_0) (fig.6.7) is in conformity with the predictions of equation (6.50). In each case, there is an identical cut-off or transition frequency. Below cut-off, these parameters show a monotonic decrease while above they increase rapidly. Such a two power-law behaviour has been frequently observed in amorphous materials [Goswami et al. 1973, Jonscher 1976, Mott and Davis 1979, Long 1982]. Equation (6.53) indicates that with increasing temperature (as R_p decreases), $\omega_{\min}$ should shift towards higher values - a feature partially observed in Cu-GeO₂ thin films (see figs. 6.6 and 6.7).

Equation (6.47) predicts the behaviour of C_s , as observed in figs. 6.4 and 6.5. At given temperature, $D (= 1/\omega C_p R_p)$ decreases with increasing frequency leading to a decrease in C_s whereas at given frequency, D increases with rising temperature leading to an increase in C_s .

6.6.2 Variation of AC conductivity with frequency and temperature

The magnitude of the conductance G_p at a given temperature and frequency was found to lie in the range 0.16 to 15 nS. Since the sheet resistance (R_s) of the material is very high (about 10^{10} ohms at room temperature) and the lead resistance r very low (about 5 ohms), a simple impedance calculation shows that G_p is effectively equal to $1/R_p$. Taking the given geometry of the samples, the measured conductivity $\sigma(\omega)$ was calculated using the relation:

$$\sigma(\omega) = (d/R_p A)$$

However, it is known that [Long 1982, Elliot 1987] AC loss is always accompanied by a DC component at $T > 0$ K. As a result the DC component must be carefully subtracted from $\sigma(\omega)$ to obtain $\sigma_1(\omega)$. To this end, the zero-frequency DC conductivity was measured in the same temperature range i.e. 150 to 425 K.

At high temperatures and low frequencies the DC conductivity becomes comparable with $\sigma(\omega)$, and therefore, $\sigma_1(\omega)$ can be extracted from $\sigma(\omega)$ using equation (6.2). But at lower temperatures ($T < 303$ K), the AC conductivity $\sigma_1(\omega)$ completely dominates the DC conductivity at all frequencies and, as such, no subtraction is necessary. Fig. 6.8 shows the frequency dependence of $\sigma_1(\omega)$ at different temperatures. Two distinct frequency regions similar to those of figs. 6.6 and 6.7 are visible. This

behaviour suggests that the single universal law (eqn. 6.1) may, in fact, be a combination of two power-laws, respectively, below and above the cut-off frequency f_m . Values of the frequency exponent s below 1 may be observed at lower frequencies while values greater than 1 may correspond to typical high frequency behaviour. It will be argued in sections (6.7.1) and (6.7.2) that such behaviour actually represents two dielectric processes: relaxation due to QMT and resonant process, below and above f_m , respectively.

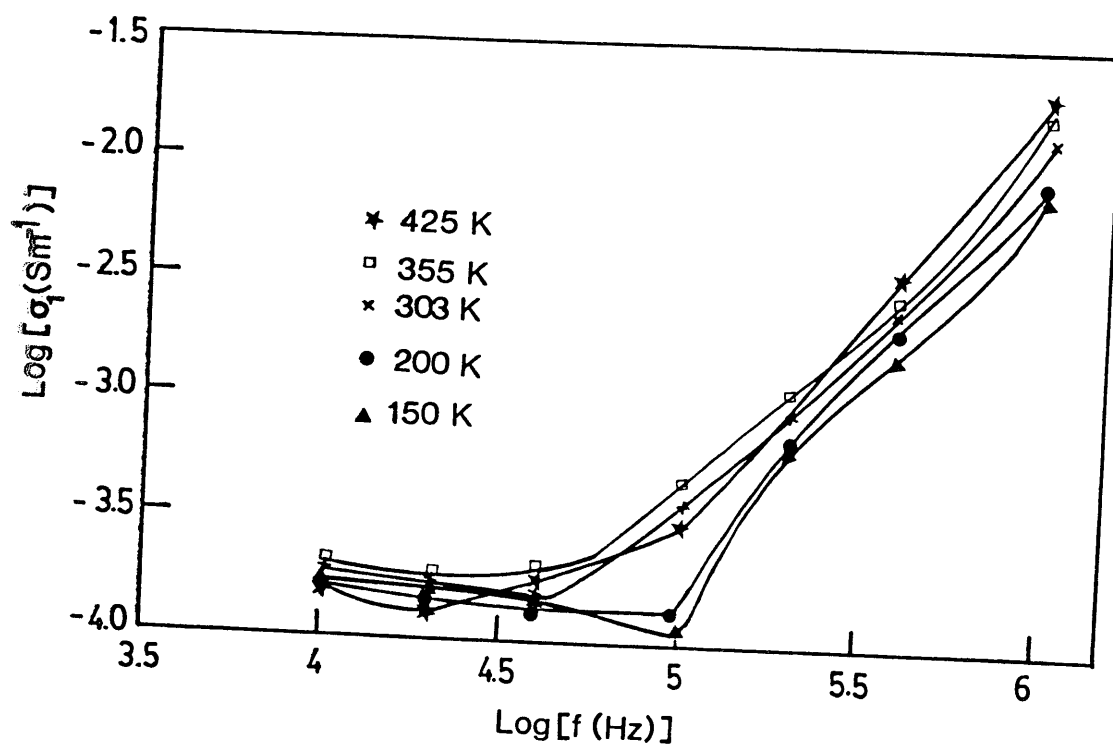


Fig.6.8: Frequency dependence of $\sigma_1(\omega)$ at different temperatures.

s was determined from the slopes of fig. 6.8, and, with values determined earlier from the slopes of fig. 6.7, an average value was calculated. Table 6.1 shows the average values of s as a function of frequency in the two frequency regions. At low temperatures (150 to 200 K), conductivity decreases slightly as frequency is increased to 4×10^4 Hz leading to a negative value of s (-0.25 to -0.19). At $T > 200$ K, $\sigma_1(\omega)$ shows a slight increase as frequency is increased towards the cut-off value; s becoming positive in the range 0.29 to 0.51.

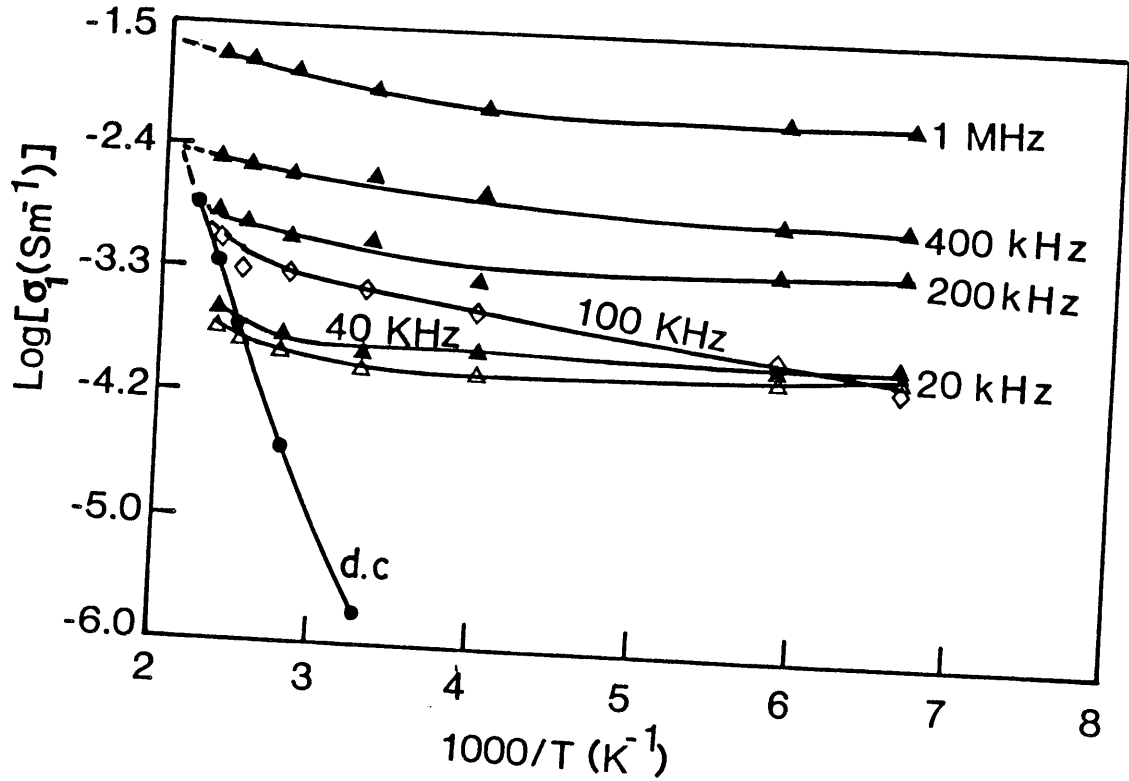


Fig.6.9: Temperature dependence of $\sigma_1(\omega)$ at different frequencies.

At higher frequencies ($f = 10^5$ to 10^6 Hz) fig. 6.8 shows that $\sigma_1(\omega)$ increases rapidly with frequency at all temperatures. Over this range, AC conductivity seems to follow a second power law (i.e. $\sigma_1(\omega) \propto \omega^2$) with s lying in the range 1.75 to 1.91.

Fig.6.9 shows the temperature-dependence of $\sigma_1(\omega)$ at different frequencies. At low temperatures and at frequencies below f_m , the AC conductivity shows a very weak temperature-dependence; the temperature exponent n lies in the range 0.10 to 0.14. The resulting curves further indicate that the AC loss can be written as,

$$\sigma_1(\omega) \approx \sigma_0 e^{-W/KT} \quad (6.54)$$

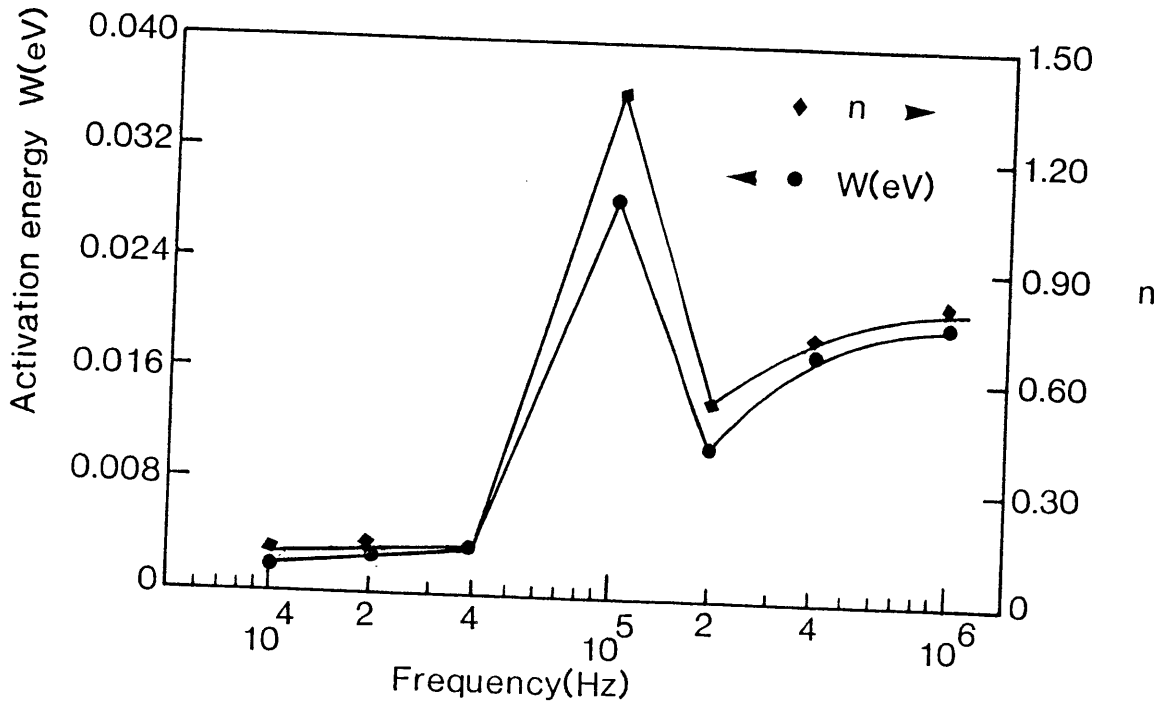


Fig.6.10: Activation energy (W) and temperature exponent (n) plotted as a function of frequency. At the cut-off frequency (10^5 Hz) both W and n curves show a maximum indicating that above that frequency a different dielectric process may be in operation.

The relaxation time is given by equation (6.17). From the data of fig. 6.9, W was calculated using equation (6.54) in the range 0.18×10^{-2} to 0.30×10^{-2} eV. At 10^5 Hz, $\sigma_1(\omega)$ shows a stronger temperature-dependence, with $n = 1.40$ corresponding to increased activation energy of 0.03 eV. Above the cut-off frequency, the temperature-dependence is seen to decrease, with a consequent decrease in activation energies. The values of n , W and related parameters at different frequencies and at temperature 150 K are listed in Table 6.2. Fig. 6.10 demonstrates the striking correlation between n and W as a function of frequency.

The two power-law behaviour of the AC loss data below and above the cut-off frequency may be analysed in a similar fashion to that of $\tan\delta$. We assume that C_p is the inherent capacity element of the circuit in fig.6.3a unaffected by frequency and temperature. R_p is the discrete resistance element due to the dielectric film and is affected by temperature and frequency. Fig. 6.3a represents a physical situation whereby AC conductivity is affected by a finite contribution from DC conductivity [Jonscher 1983, Long 1982]. The parallel mode admittance $Y_p(\omega)$ is given by

$$Y_p(\omega) = G_p(\omega) + j\omega C_p \quad (6.55)$$

where the conductance $G_p(\omega) \approx 1/R_p$ that does not include any contribution from lead and contact resistance r . It is widely believed, however, that the effective conductance (G_{eff}) of the circuit in fig.6.3b should have a contribution from r and that it is this effect which will lead to the $s > 1$ behaviour of G_{eff} [Lakatos et al. 1971, Street et al. 1971, Goswami et al. 1973, Long 1982]. In order to investigate this behaviour, we begin by defining an effective admittance for the circuit in fig. 6.3b,

$$Y_{eff}(\omega) = G_{eff}(\omega) + j\omega C_{eff}(\omega) = 1/Z_{eff} \quad (6.56)$$

Substituting Z_{eff} from equation (6.45), equation (6.56) can be rewritten as

$$\begin{aligned} Y_{eff}(\omega) &= \frac{1 + j\omega C_p R_p}{r + j\omega C_p R_p + R_p} \\ &= \frac{(r + R_p) + \omega^2 C_p^2 R_p^2 r + j\omega C_p R_p (r + R_p)}{(r + R_p)^2 + \omega^2 r^2 C_p^2 R_p^2} \end{aligned} \quad (6.57)$$

Equating the real parts of equations (6.56) and (6.57), we obtain,

$$G_{eff}(\omega) = \frac{(r + R_p) + \omega^2 C_p^2 R_p^2 r}{(r + R_p)^2 + \omega^2 r^2 C_p^2 R_p^2} \quad (6.58)$$

Equation (6.58) has two important consequences. In the lower frequency region (e.g. $\omega < \omega_{min}$, eqn.(6.53)) and assuming that $r/R_p \ll 1$ in all cases, equation (6.58) becomes,

$$G_{eff}(\omega) = (1/R_p^2)/(1/R_p) = \frac{1}{R_p} = G_p(\omega) \quad (6.59)$$

Equation (6.59) suggests that at lower frequencies effective conductance is not affected by the series lead resistance. This inturn leads to the $s \leq 1$ behaviour of the effective conductance. However, when the frequency is increased towards ω_{min} so that $\omega_{min}^2 C_p^2 R_p^2 r = 1$ (eqn.(5.53)) condition is satisfied, then G_{eff} begins to rise above G_p . This can be seen by dividing the numerator and denominator of equation (6.58) by R_p^2 . In the limit $r/R_p \ll 1$, equation (6.58) can be rewritten as

$$G_{eff}(\omega) = \frac{(1/R_p) + \omega^2 C_p^2 r}{1 + \omega^2 C_p^2 r^2} \quad (6.60)$$

Using $\omega_{min}^2 C_p^2 R_p r = 1$, the above expression becomes, in the limit $r/R_p \ll 1$,

$$G_{eff}(\omega) = G_p(\omega) + \omega^2 C_p^2 r \quad (6.61)$$

As mentioned earlier $G_p(\omega)$ will have a contribution from DC conductance (see eqn. (6.2)). Separating AC and DC contributions in $G_p(\omega)$, equation (6.61) can be rewritten as

$$G_{eff}(\omega) = G_{dc}(T) + G_1(\omega) + \omega^2 C_p^2 r \quad (6.62)$$

We recall that $G_1(\omega)$ is given by equation (6.1). Equation (6.62) then becomes,

$$G_{eff}(\omega) = G_{dc}(T) + \omega^s T^m + \omega^2 C_p^2 r \quad (6.63)$$

Equation (6.63) clearly predicts a two power-law behaviour for the effective conductance $G_{eff}(\omega)$. At lower frequencies, the contribution from r can be neglected for very low capacitive materials. In this case, the first two terms are expected to dominate the conductance, with s taking values in the range $0 < s \leq 1$. The temperature of observation at a given frequency determines which of these two terms contributes significantly to the overall conductivity. At higher frequencies ($\omega \geq \omega_{min}$), the effect of r becomes significant and hence the third term may dominate the overall conductivity, raising the possibility of photon-activated electronic transition processes, as discussed in section (6.4.4).

It appears that the two power-law behaviour (eqn. 6.63) is generally followed in the present investigation; at frequencies below $f_m (\approx 10^5 \text{ Hz})$, s lies in the range

$-0.25 \leq s \leq 0.51$ whereas above f_m the AC conductivity shows a quadratic behaviour with s (1.75 to 1.91) slightly deviating from the predicted value of 2. It will be argued in sections (6.7.1) and (6.7.2) that this two power-law behaviour reflects two fundamentally different dielectric processes in operation. Furthermore, though the universal equation (6.1) does not predict a negative frequency exponent for semiconductor materials, it will be shown in section (6.7.1) that such a behaviour is not unrealistic.

6.6.3 The loss minima and the activation energy

Fig. 6.6 and 6.7 clearly indicate well-defined loss minima at around 10^5 Hz, which shifts slightly to higher values (2×10^5 Hz) with increasing temperature. This suggests that the microscopic relaxation time must be given by equation (6.17) and that the cut-off frequency f_m should follow an activated relationship of the form,

$$f_m = \frac{1}{\tau_{ot}} e^{-W/KT} \quad (6.64)$$

Fig. 6.11 shows the loss-minimum frequency plotted against $1000/T$. The resulting straight line implies that equation (6.64) is obeyed, with constant characteristic relaxation time τ_{ot} lying in the narrow range 10^{-7} to 10^{-6} s. Corresponding to these values, an average activation energy W equal to 0.019 eV can be determined. This compares favourably with 200 kHz activation energy: $W=0.011$ eV, obtained from fig.6.9 and reproduced again in fig. 6.11 for the sake of clarity.

The large values of τ_{ot} are quite unexpected: in many amorphous materials τ_{ot} is the inverse of Debye frequency i.e. 10^{-13} to 10^{-12} s. However, it will be argued in section (6.7.1) that such large values of τ_{ot} are not unrealistic; infact they are consistent with the

predictions of small polaron tunneling and resonant processes.

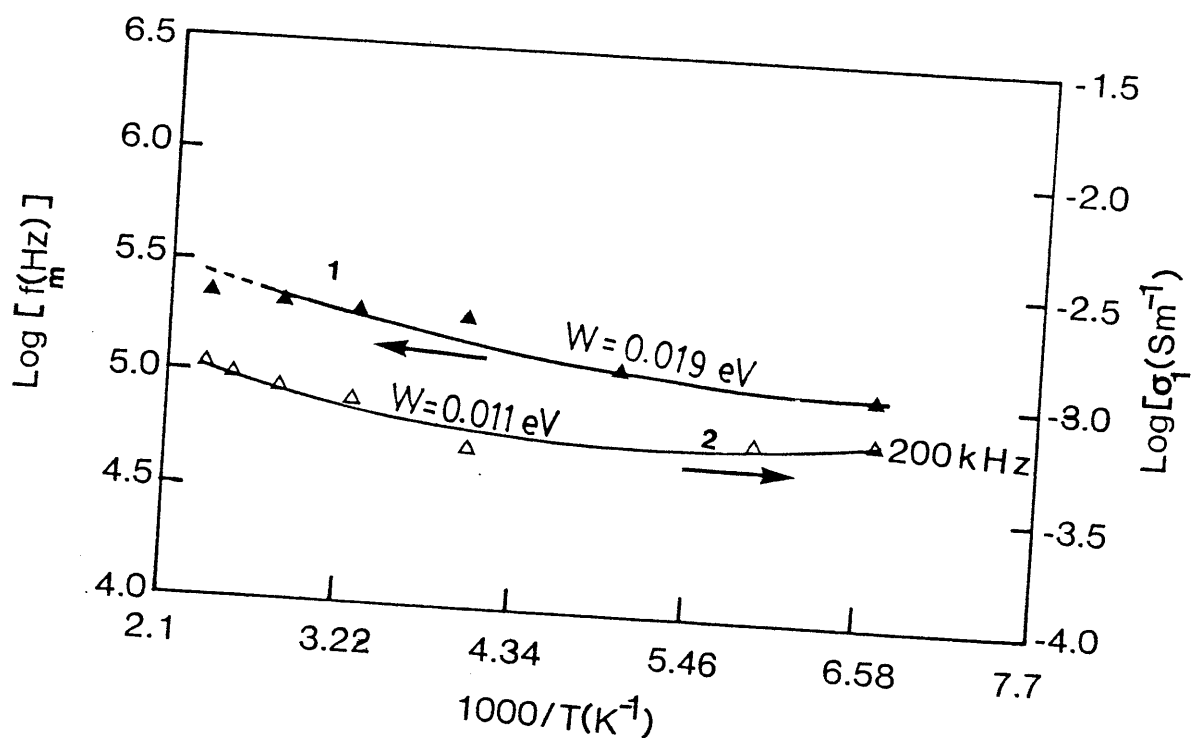


Fig.6.11: Dependence of the cut-off frequency f_m on reciprocal temperature (curve 1) and variation of $\sigma_1(\omega)$ at 200 Hz with $1/T$ (curve 2).

Table 6.1 The frequency exponent s calculated from figs. 6.8 and 6.7 at different frequency regions. $\bar{s}$ represents the average value used in fig. 6.12.

Temp (K)	10 ⁴	to	10 ⁵ Hz	10 ⁵	to 10 ⁶	Hz
	s fig. 6.8	($s-1$) fig. 6.7	$\bar{s}$	s fig. 6.8	$s-1$ fig. 6.7	$\bar{s}$
150	-0.2	-1.3	- 0.25	1.82	1	1.91
170	-0.21	-	- 0.21	1.74	-	1.74
200	-0.22	-1.15	-0.19	1.61	0.77	1.69
250	0.35	-0.75	0.30	1.50	0.65	1.58
303	0.42	-0.59	0.41	1.39	0.70	1.54
355	0.45	-0.56	0.44	1.45	-	1.45
400	0.62	-0.61	0.50	1.69	0.82	1.75
425	0.63	-0.61	0.51	1.81	0.70	1.76

Table 6.2 Values of the AC loss parameters at 150 K

f (kHz)	n at 150-425K	W (eV) at 150-425K	σ_1 ($S m^{-1}$) at 150K	ϵ' / ϵ_0 at 150K	ϵ'' / ϵ_0 at 150K
10	0.10	1.8×10^{-3}	1.7×10^{-4}	14.0×10^3	294.9
20	0.10	2.7×10^{-3}	1.6×10^{-4}	14.1×10^3	136.7
40	0.14	3.0×10^{-3}	1.5×10^{-4}	14.1×10^3	70.3
100	1.40	30×10^{-3}	1.1×10^{-4}	13.9×10^3	9.8
200	0.57	11×10^{-3}	6.5×10^{-4}	14.1×10^3	56.2
400	0.70	18×10^{-3}	15×10^{-4}	14.1×10^3	70.4
1000	0.78	20×10^{-3}	79×10^{-4}	13.9×10^3	140.0

6.7 The Conduction mechanism

In earlier investigations (sections(4.4.2) and(5.7.1)) [Al-Saie et al. 1993, Rahman et al. 1994] on Cu-GeO₂ thin amorphous films, it was postulated that the Fermi level is pinned at the middle of the energy gap and that the donor impurity states lie 0.01 eV above the Fermi level. Below 355 K, DC conduction was identified with hopping of small polarons through impurity states whereas above 355 K contributions from band conduction was predicted. These observations strongly suggest that there exists a large number of localized states close to the Fermi level and that the DC conductivity originates from hopping conduction mechanism via these states below 355 K. It is interesting to explore if the same mechanism is responsible for the AC conduction.

AC conduction mechanism is usually interpreted in terms of various models described in sections (6.4.1), (6.4.2), (6.4.3), (6.4.4) and (6.4.5). In general, it is difficult to establish which of these models best determines the conduction process. It has been pointed out that the dielectric response of many materials is complicated by the presence and overlap of different polarisation processes, and that a single universal law (eqn 6.1) may not represent the true behaviour of most materials [Jonscher 1983]. A careful study of the temperature dependence of s is expected to be useful in this context. The AC loss data in the present study are clearly divided into two distinct frequency regions. Each region may correspond to fundamentally different processes of dielectric polarisation. In the following two sections these processes and their physical implications are further examined.

6.7.1 The low frequency region (10^4 to 10^5 Hz)

The conductivity $\sigma_1(\omega)$ (fig. 6.8) is seen to reach a minimum as does the loss factor $\varepsilon''/\varepsilon_0$ (fig. 6.7) at a frequency given by equation (6.64). This behaviour results in negative values of s in the temperature region (150 to 200 K). One implication of the negative value for s is that the dielectric loss decreases rapidly with frequency and reaches a sharp minimum. At this cut-off frequency the tunneling distance R_0 (eqn. 6.23), and hence $\sigma_1(\omega)$ (eqn. 6.20) tend to zero. These features are in conformity with those predicted by small polaron tunneling model (see section (6.4.2)).

The temperature dependence of s is shown in fig. 6.12 (curve a); in this frequency region, s is an increasing function of temperature and attains positive values above 200 K. This behaviour also appears to be consistent with Long's small polaron tunneling model (see eqn. 6.26). Taking the values of W from Table 6.2 and noting that $\tau_{ot} \approx 10^{-7}$ to 2.63×10^{-6} s, s was calculated using equation (6.26). The dotted line in fig. 6.12 represents these calculated values, which are in excellent agreement with experimental solid-line.

However, equation (6.26) also suggests a frequency-dependent s which is not apparent in the narrow frequency region 10^4 to 10^5 Hz. A detailed analysis shows that s does change as the frequency is increased in narrow steps of 10, 20 and 40 kHz. This change, $\Delta s = 0.02$, is small at low temperatures, but increases to 0.116 at higher temperatures ($T > 200$ K). However, the frequency range in the experiment was so narrow that no frequency-dependence of s was observable. Working in a coplanar geometry, a similar behaviour of increasing s with temperature in

a:Ge and a:InSb was reported by Narasimhan et al. [1976].

The Austin-Mott QMT model (see section (6.4.1)) predicts that $s(<0.8)$ is temperature-independent and decreases with increasing frequency. To obtain the values of $s<0.8$, one has to assume unphysically low values of characteristic relaxation time ($\approx 10^{-13}$ s). These features are contradicted by the present experimental observations. The Pike-Elliott CBH model, (see section (6.4.5)) on the other hand, predicts that s can have values lower than 1.0 at high temperature and should increase as the temperature is lowered (eqn.6.42). Our experimental results show just the opposite trend. Both these models (QMT and CBH) cannot, therefore, explain our results.

The temperature dependence of $\sigma_1(\omega)$ (fig.6.9) in this frequency region (10^4 to 10^5 Hz) is weak, with n taking values 0.10 to 0.14. Such weak temperature dependence of AC loss has been reported in many amorphous materials [Hauser 1983, 1985, Long 1982, Elliot 1987]. The small polaron tunneling model does predict a relatively weaker-temperature dependence of AC conductivity (eqn. 6.27) compared to the QMT (eqn. 6.20) and CBH models (eqn. 6.43). Around the cut-off frequency $\approx 10^5$ Hz, n increases sharply to 1.4 (see fig. 6.10). This strong temperature-dependence suggests a stronger activated process when the dielectric loss minimum is reached. This may also signal the onset of a different type of conduction mechanism above 10^5 Hz as will be discussed in the next section.

6.7.2 High frequency behaviour ($f > 10^5$ Hz)

Fig. 6.12 (curve b) shows that s starts to decrease from a maximum value of 1.91, reaches a minimum value of 1.45 at 355 K before increasing again to 1.76 at 425 K. A minimum value of s has been observed in sputtered Germanium [Long 1982] and in binary V_2O_5 - P_2O_5 glasses [Murawski 1984]. However, in both of these cases s decreases from a maximum value of 1.0 in agreement with Long's [1982] large polaron tunneling mechanism (see section (6.4.3)). Viadi et al. [1969] had observed an s of 1.75 in MgP_C films and attributed this value to hopping conduction. In a more recent work, Rahman et al. [1987] observed an s of 2 in SiO/SnO_2 films in the high frequency region $f (> 10^5$ Hz). They attributed such phenomena to CBH-type hopping mechanism.

However, relaxation processes associated with defect centres that are the foundations of the QMT and CBH models cannot account for the super-linear (i.e. $s \approx 2$) behaviour of s [Mott et al. 1979, Long 1982, Elliot 1977, 1987]. Because of this, the possibility of a resonant process contributing to the AC loss becomes stronger. Equations (6.36) and (6.63) do predict this kind of behaviour at high frequencies. Taking a typical value for the overlap integral I_0 equal to 5 to 10 eV [Elliot 1987] and the cut-off frequency 10^5 Hz, above which a super-linear behaviour of AC conductivity is predicted to occur, equation (6.36) gives s equal to 1.84. This value is quite close to the observed value of 1.91. The logarithmic term in equation (6.36) varies weakly as a function of frequency leading to a slight variation in s , $\Delta s \approx 0.015$. Hence, fig. 6.12 (curve b) shows that s is almost frequency-independent as was observed in the lower frequency region (curve a).

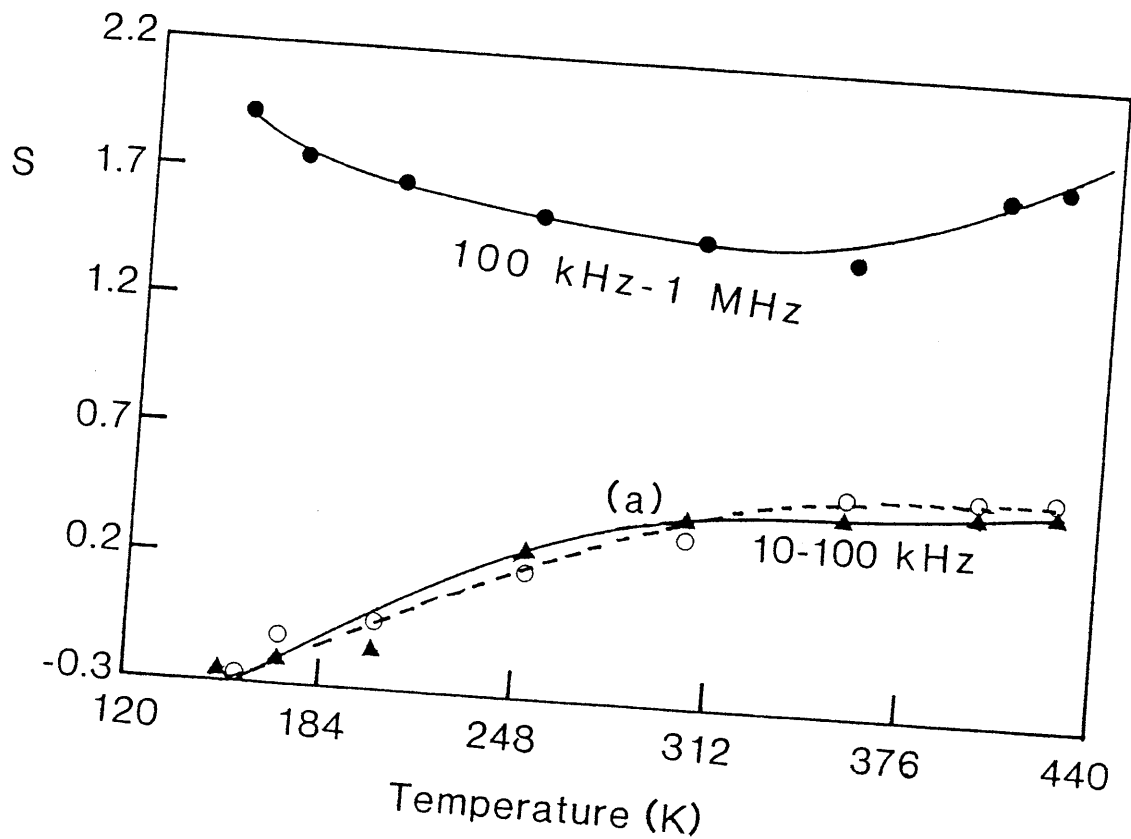


Fig.6.12: Temperature dependence of the exponent s at different frequency regions: (a) experimental curve in the range 10^4 to 10^5 Hz. The dotted line is calculated using equation (6.26). (b) 10^5 to 10^6 Hz.

It appears that, in the high frequency region ($f > 10^5$ Hz), the AC conductivity of Cu-GeO₂ films is dominated by photon-activated resonant absorption processes discussed in section (6.4.4).

It is interesting to note that the DC and AC conductivity do not seem to arise from the same basic processes and, therefore, extraction of $\sigma_1(\omega)$ from the total measured conductivity $\sigma(\omega)$ using equation (6.2) appears to be a valid assumption.

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

The aim of the present work was to investigate the DC and AC electrical conduction mechanisms in electron beam evaporated Cu-GeO₂ thin cermet films. For this purpose optical, DC, Hall effect and AC measurements were performed on number of films with varying thicknesses and compositions. However, the main emphasis was to explore a fixed composition (e.g. 30 at.wt.% Cu films) with identical deposition conditions in order to allow ready comparison of the results.

In the course of this investigation, the author had to prepare the thin film laboratory starting from scratch, by installing electron beam evaporation system in the coating unit, by installing and calibrating quartz crystal monitor, by designing and fabricating the van der Pauw conductivity/Hall effect set up, and by fabricating a photosensor for the in-situ optical thickness measurements.

One could extend the present work by studying films prepared by different deposition techniques at different deposition parameters, particularly films prepared at elevated substrate temperatures. Theory of nucleation and growth suggests that at higher substrate temperatures, the adhesion of the evaporant particle to the glass substrate improves significantly. This in turn affects the microstructure of the films, resulting in significant changes in its electronic transport properties.

7.1 Optical absorption

7.1.1 Summary

In the present study optical parameters such as the optical energy gap, the width of the tail of localized states in the band gap, the refractive index and the extinction coefficient were measured in the photon energy range 1.0 eV to 5.0 eV. The aim of these measurements were to obtain information about the band structure of Cu-GeO₂ thin films. X-ray diffraction measurements were performed to confirm the amorphous nature of the materials. This was further supported by differential scanning calorimetry (DSC) which showed that the amorphous nature of the samples persisted with no evidence of phase transition up to 500°C.

Infrared (IR) studies on as deposited samples fail to show any interference fringes in the range 400 cm⁻¹ to 4600 cm⁻¹. Furthermore, the IR absorption spectra suggests that GeO₂ is the dominant matrix in Cu-GeO₂ cermet system upto atleast 30 at.wt.% Cu concentration. This conclusion was further strengthened by DC conductivity and Hall effect studies where it has been conclusively established that small polaron hopping conduction occurs between two Cu-sites seperated by the dominant matrix GeO₂.

Optical transmission measurements showed that the films were highly transparent (85 to 90 %) in the visible region. The ultraviolet (UV) and visible (VIS) results show that the optical energy gap increases with increasing thickness but decreases with increasing Cu concentration and that the absorption was due to indirect transitions in K-space. The increase in E_{opt} with increasing thickness and decreasing Cu concentration is attributed to a reduction of defect states. The general

feature of the absorption edge remains similar for both unannealed and annealed films, but annealing has the effect of decreasing E_{opt} . The optical energy gap of amorphous GeO_2 films (2.80-2.86 eV) is found to be higher than those for the Cu- GeO_2 system (1.30 to 2.24 eV) suggesting that incorporation of Cu in the matrix of GeO_2 introduces defect states leading to a reduction in E_{opt} .

For each film, it was found that the absorption coefficient $\alpha(\nu)$ increases exponentially with photon energy in the range (1-3 eV). This behaviour suggested that Urbach rule (eqn 3.17) was being followed. The width of the band tail-states was found to vary significantly with thickness and compositions in the range 0.60 to 1.23 eV. These observations suggested that the Urbach behaviour might originate from electronic transitions between localized states in agreement with Tauc [1970] model.

The refractive index $n(\lambda)$ and the extinction coefficient $K(\lambda)$ were studied as a function of photon energy. Both parameters showed a sharp increase in their respective values beyond certain photon energy. In particular, $K(\lambda)$ increases rapidly beyond 2 eV while $n(\lambda)$ shows sharp rise in the values (2.5 to 4.5) in the same spectral region. It is believed that these identical transition points in the $K(\lambda)$ and $n(\lambda)$ plots may mark the approach of the band gap.

7.1.2 Suggestions

- An interesting experiment would be to conduct optical absorption and transmission studies on Cu- GeO_2 thin films at percolation threshold i.e. at which transition from dielectric to metallic regimes takes place. Increased Cu concentration may introduce higher compositional disorder

and metallic impurities both of which will affect the energy band structure and the conduction mechanism.

- Studies of the detailed temperature dependence of the bandgap and the band tails would give important information about the nature and causes of bandgap shifts, and the Urbach behaviour. In addition, detailed theoretical calculations supported by accurate experimental data will help to understand the complex electron-electron interactions and impurity scattering mechanism responsible for bandgap shifts.

7.2 DC Conduction Mechanism

7.2.1 Summary

The two-probe method was employed to study the thickness dependent electrical properties of 30 at.wt.% Cu films in the temperature range 323 to 573 K. At temperatures below 323 K, the data showed a significant amount of scattering and uncertainty. As a result, no definite trend of the conduction behaviour could be established. Above 323 K, it was found that the DC conductivity was well defined by an Arrhenius-type relation (eqns. 4.3 and 4.6) in which the activation energy was single-valued. The thermal-activation energy was found to be 1.08 eV, 1.01 eV and 0.68 eV for the films with thicknesses 227, 340 and 407 nm respectively. The activation energy decreases systematically with increasing film thickness. Furthermore, it was noticed that incorporation of Cu in the matrix of GeO_2 has the effect of decreasing the activation energy. On comparison of E_a with E_{opt} (i.e. $E_a < 1/2 E_{\text{opt}}$), it was deduced that an impurity band existed within the mobility gap. A detailed analysis of the conductivity dependence on temperature suggests that conduction occurs between two island states due to thermal-activation, and that Neugebauer-Webb [1962] and

Hill-Coutts [1977] models best describe the conduction mechanism in the high temperature ($T > 323\text{K}$) range.

The four-probe van der Pauw technique was employed to study the composition dependent electrical properties. The slopes of the conductivity curves for 5 to 30 at.wt.% Cu films were seen to continuously change with temperature in the range 307 to 425 K. This behaviour suggested that the conductivity was an exponentially activated process and that a single Arrhenius type exponential could not be fitted over the entire temperature range. It was also observed that the conductivity sharply rises beyond a certain temperature, known as the critical temperature T_c . Above T_c , the two and four probe methods (for 407 nm and 410 nm thick films containing 30 at.wt.% Cu) both yield almost the same value of the activation energy, e.g. 0.68 eV and 0.66 eV respectively. Below T_c , the curves gradually leveled out indicating a very weakly-activated process with values of the activation energy lying in the range 0.10 to 0.25 eV. This suggests that at lower temperature range, conduction occurs due to hopping of carriers through localized states. The combined knowledge of optical absorption, DC conductivity and Hall effect results indicates the existence of two groups of localized states in the mobility gap. The first group is localized within a tail width of 0.64 eV below E_c while the second group is localized in the central region (near the Fermi level) around 0.01 eV below the tail states.

Above T_c , the abrupt jump in the activation energies and prefactor σ_0 indicates that conduction occurs due to transport of carriers via extended states. The existence of a sharp transition point in the conductivity curves may imply a Nagel-type mixed conduction process with two well defined activation energies. However, a critical examination of the four-probe conductivity curves shows

that the activation energy changes continuously and uniformly with temperature implying that small polaron model best describes the conduction mechanism.

7.2.2 Suggestions

- To detect sharp changes in the conductivity curves (Two-channel model) or continuously varying slopes (small polaron model) with greater accuracy, data over an extended temperature ranges may be required. This was not possible in this work due to experimental limitations. Therefore, one can repeat and re-examine the entire issue of DC conductivity for higher temperature range.
- Thermopower measurements on the samples will further contribute to the understanding of electrical transport mechanisms. It is generally believed that when transport mechanism changes from one channel to the other, the behaviour of the thermopower will depend on the form of the conductivity curves [Le Comber et al. 1972, Nagels et al. 1973, Elliot 1990]. If a sharp change in the conductivity curve is observed, one expects a sudden rise in thermopower around the critical temperature T_c . Furthermore, the thermopower activation energy is often found to be less than the corresponding DC activation energy. Causes of this apparent discrepancy has not been resolved and requires further theoretical and experimental clarity.
- In section (4.4.3), a least-squares fit of the conductivity data does not yield entirely linear lines. This may be due to shifting Fermi energy (E_F) with temperature. Consequently, this introduces significant uncertainty and errors in our understanding of the energy band structure. Hence, this problem demands further investigation.

7.3 Hall effect and magnetoresistance studies

7.3.1 Summary

van der Pauw conductivity and Hall effect were investigated on 5 to 30 at.wt.% Cu films in the temperature range 307 to 413 K. A sign reversal in Hall mobility was observed for all the three samples. The Hall mobility shows a maximum at a critical temperature identical to that of the DC conductivity T_C . In the lower temperature range ($T < T_C$), the conductivity is weakly activated but Hall mobility shows a rapid increase with increasing temperature, indicating that mobility is associated with the hopping of carriers in the localized states. In the higher temperature range ($T > T_C$), the Hall mobility decreases and the DC conductivity increases sharply with increasing temperature. A detailed analysis of the intrinsic conduction mechanism at $T \geq T_C$ suggests that carrier concentration may be the principal factor governing the conductivity via extended states. Lattice scattering at higher temperatures is believed to be the cause of decreasing mobility.

The hopping activation energy W calculated from the mobility curves has values in the range 0.090 to 0.098 eV. Such low values, together with the fact that they vary little between the samples, that mobility curves show maxima and that the values of the prefactor σ_{01} in equation (4.44) remain almost constant between the samples, strongly suggest that small polaron model best describes the conduction mechanism in this material.

For 5 and 20 at.wt.% Cu films, it is believed that conductivity is dominated by a mixed conduction process below the critical temperatures 375 and 367 K, respectively. For 30 at.wt.% Cu film, electrons are the major carriers upto 389 K indicating that with increasing

Cu content mixed conduction diminishes and the material tend to become unipolar.

Magnetoresistance (M) studies were performed in a static magnetic field of 20 to 180 mT. The signs of M were consistent with the signs of Hall mobility further confirming the mixed conduction process hypothesis.

7.3.2 Suggestions

- The sign discrepancy between the Hall coefficient and the thermopower remains an outstanding problem. Differences in the sign of the carriers, as determined from thermopower and Hall effect measurements have been reported for many amorphous materials [Mott et al. 1979, Elliot 1990]. For low mobility transport, the sign of the Hall coefficient may be anomalous i.e not the same as that of the carrier. It frequently manifests a sign opposite to that of the thermopower. It is generally believed that sign of thermopower gives a more reliable indication of whether the conduction is dominated by holes or electrons. While two-channel and small polaron models successfully account for this sign anomaly in a wide variety of materials, the underlying approaches of these models are radically different. It was pointed out earlier (see sections (7.1.2) and (7.2.2)) that true values of E_{opt} and E_a could not be obtained due to temperature-dependent shifts of E_F . Thermopower results in conjunction with DC conductivity and Hall effect data can obviate these problems [Elliot 1990].
- Optical absorption, DC conductivity and Hall effect experiments in this work did not reveal much about the nature of defect states within the mobility gap. Conductivity (or drift) mobility measurements can yield valuable information on the energies and distribution of

gap states which can be analyzed in terms of various models of defect states [Street et al. 1975, Mott et al. 1975, Mott et al. 1977].

7.4 AC electrical conductivity and dielectric properties

7.4.1 Summary

AC electrical properties of 410 nm thick 30 at.wt.% Cu-70 at.wt.% GeO₂ cermet films were studied in the frequency range 10^4 to 10^6 Hz and temperature range 150 to 425 K. Capacitance shows a slight decrease in values with increasing frequency. At all frequencies, capacitance increases with increasing temperature. The AC conductivity $\sigma_1(\omega)$, the loss tangent $\tan\delta$, and the dielectric loss (ϵ'/ϵ_0) all show striking minima around a cut-off frequency of 10^5 Hz indicating two fundamentally different dielectric processes in operation. In the lower frequency range ($f \leq 10^5$ Hz) equation (6.1) is obeyed with s (-0.25 to 0.51) increasing as a function of temperature and n (0.10 to 0.14) showing a very weak temperature dependence. At low temperatures (150 to 200 K), s becomes negative indicating that AC conductivity decreases, reaching a minimum as the tunneling distance (R_ω) approaches a cut-off value. This behaviour is predicted at $f_m \approx 10^5$ to 2×10^5 Hz corresponding to a narrow distribution of constant characteristic relaxation time 10^{-7} to 10^{-6} s. These features are found to be consistent with Long's small polaron tunneling model. In the higher frequency region ($f \geq 10^5$ Hz), both $\sigma_1(\omega)$ and (ϵ'/ϵ_0) increase sharply leading to the ω^2 behaviour, which suggests that conduction occurs via the Mott-Davis type photon-activated resonant process.

Two interesting features of this work are that a single universal power law embodied in equation (6.1) does not seem to describe the conduction mechanism in the entire

frequency range and that AC and DC conductivity do not seem to arise from the same physical processes.

7.4.2 Suggestions

- Negative values of the frequency exponent s (at low temperatures) appears to be due to the well defined loss minima. Physically it would imply that as $\sigma_1(\omega)$ approaches a cut-off value, the tunneling distance R_ω tends to become zero which appears to be unrealistic [Elliot 1987]. Therefore, a detail studies in this or other non-crystalline materials would be needed to further investigate this behaviour.
- Since s shows a minimum at high frequency (fig. 6.12), the possibility does remain that large polaron tunneling process (see section (6.4.3)) is responsible for high frequency transport mechanism. However, this model fails to account for the superlinear ($s > 1$) behaviour of the AC conductivity observed in Cu-GeO₂ films. This, therefore, asks for further experimental investigations.
- The present work was carried out in coplanar geometry in relatively high frequency range. One could investigate the validity of the universal power law (eqn. 6.1) and the two power law behaviour (eqn. 6.63) in sandwich geometry for extended frequency range, say 10 to 10⁶ Hz. At present no single theory exists that explains the transition from low frequency behaviour to high frequency behaviour. It would appear that the mechanism yielding the highest contribution to the AC loss should be determined experimentally. Above and below the cut-off frequency, one should be able to detect the transition from one mechanism to another.
- Other phenomena which may be studied are the electric and electrothermal breakdown of a dielectric. These

studies are of extreme importance in electrical insulation engineering.

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