

**Thermal transport, photoconduction and electrical switching
in selected chalcogenide glasses exhibiting
carrier type reversal**

**Thesis submitted to
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in partial fulfilment of the requirements for the award of the degree of
DOCTOR OF PHILOSOPHY**

By

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CERTIFICATE

Certified that the work presented in this thesis is based on the bona fide work done by Mr. Rajesh R under my guidance in the Department of Instrumentation, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for the award of any degree.

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2nd September, 2001



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Dr. Jacob Philip

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DECLARATION

Certified that the work presented in this thesis is based on the original work done by me under the guidance of Dr. Jacob Philip, Professor, Department of Instrumentation, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for the award of any degree.

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Rajesh R

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PREFACE

Non-crystalline or amorphous alloys form an important class of materials from the point of view of fundamental condensed matter research as well as technological applications. They differ from their crystalline counter parts by the absence of long-range order. Their interesting electrical, optical and magnetic properties along with the wide flexibility in preparation and composition make them unique in several applications. Like crystalline materials, non-crystalline materials can be ionic, covalent, metallic or van der Waals' bonded materials. Consequently, they can be insulating, semiconducting or metallic in nature.

Amorphous semiconductors can be generally classified into two groups as tetrahedrally coordinated semiconductors like a-Si, a-Ge etc. and chalcogenide semiconductors like Ge-Se, As-Se etc. Chalcogenide glasses contain one or more of the chalcogen elements, S, Se or Te of the sixth group of the periodic table. The four-fold coordination in Si leads to symmetrical bonding and the formation of rigid structures, while the two-fold coordination in chalcogens is highly asymmetrical and the structure gives rise to greater degree of flexibility for interatomic bonds. Like other glassy solids, these materials also possess only short-range order and because of this, the theories developed for crystalline materials cannot directly be applied to them.

Chalcogenide glasses form an important class of amorphous solids. They have very interesting physical properties and can be prepared in the bulk as well as thin film forms. One of the greatest advantages of these glasses is the composition dependent tunability of their properties, which enables one to design materials for

specific requirements. They have potential technological applications such as materials for threshold and memory switching, inorganic photoresist, xerography, IR detection and transmission etc. These materials are suitable for IR optical elements such as cell windows and prisms and as FIR beam condensers, splitters and other accessories, since they do not absorb IR radiation. Many of these glasses can be formed by the conventional melt quenching technique over a wide composition range making them suitable model systems for systematic studies on composition dependent properties.

In order to explain the features observed in the composition dependence of various properties of chalcogenide glasses, various models like random network models and topological models have been proposed. According to the chemically ordered covalent network (COCN) model, heteropolar bonding is maximized, thereby favouring chemical order. Topological models use the concept of average coordination number Z and interpret the properties of chalcogenide glasses in terms of Z .

It has long been known that intrinsic chalcogenide glasses behave like p -type semiconductors and are insensitive to 'doping' in small amounts. This behaviour is attributed to the local valence saturation of the dopant atoms. Fermi level is considered to be pinned due to the equilibrium between positively and negatively charged defect states, known as valence alternation pairs (VAPs). The presence of a large number of defect states in the band gap makes them normally insensitive to impurity doping. However, of late, it has been found that the addition of heavy elemental metallic impurities like Pb or Bi to Ge-Se glasses or Pb to In-Se glasses can enter the network as charged species, alter the concentration of VAPs and

consequently change the conduction type from p to n -type at a certain composition. This discovery has led to extensive research on these materials and to a reconsideration of the existing theories of electronic structure of chalcogenide glasses. The p to n -type change over or carrier type reversal (CTR) gets reflected in electrical transport properties such as activation energy, thermoelectric power, Hall coefficient etc. We have measured the composition dependence of thermal parameters of Pb doped Ge-Se, Bi doped Ge-Se and Pb doped In-Se systems, which are reported to undergo p to n transition as Pb/Bi doping level is varied, using photopyroelectric (PPE) and photoacoustic (PA) techniques. Specifically, we have measured composition dependence of heat capacity and thermal conductivity across the transition composition. It is found that the thermal parameters show anomalous variations at compositions corresponding to the p to n transition or carrier type reversal. We have also studied the composition dependence of photoconductivity in these systems.

Electrical switching is an interesting property exhibited by certain Te based chalcogenide glasses. It is the rapid and reversible transition between a highly resistive OFF state and a conductive ON state driven by an external electric field and characterized by a threshold voltage. Depending on the material, switching can be of threshold type or memory type. In threshold type switching, the ON state persists only while the current flows, down to a certain holding voltage, whereas in memory type switching the ON state is permanent until a suitable reset pulse is applied. We have measured the variation of thermal parameters in In-Te glass system during electrical switching using PPE technique.

Ge-As-Se is a typical ternary chalcogenide glass system. It has got one of the largest glass forming regions. We have measured the thermal parameters of this system as a function of the average coordination number and studied the effect of various topological thresholds on them.

The thesis is divided into eight chapters. In the first chapter, an overall review of amorphous semiconductors is given. It includes an introduction to chalcogenide glasses, followed by a brief discussion on the important structural models proposed for chalcogenide glasses and their electrical and thermal properties. Photoconductivity, electrical switching and carrier type reversal in chalcogenide glasses are described in detail in this chapter.

Chapter 2 presents a description of the experimental techniques used in the present investigation. Brief description of the PA spectrometer is given. Photoacoustic measurement of thermal diffusivity is described. Simultaneous measurement of thermal conductivity and heat capacity employing photopyroelectric technique is also described. Details of photoconductivity and electrical switching experiments are also given in this chapter.

Pb-Ge-Se system forms homogeneous glass in two series (i) $\text{Pb}_{20}\text{Ge}_x\text{Se}_{80-x}$ ($x = 17 - 24$) and (ii) $\text{Pb}_y\text{Ge}_{42-y}\text{Se}_{58}$ ($y = 0 - 20$). Both the series exhibit carrier type reversals; series I at $x \approx 21$, and series II at $y \approx 8$. We have measured the thermal parameters as a function of composition in this system. It is found that CTR gets reflected in these measurements. The results obtained are presented in chapter 3 of the thesis. The results are explained in terms of enhancement in carrier concentration during p to n transition.

Bi doped Ge-Se and Pb doped In-Se are two other systems which exhibit carrier type reversal. $\text{Bi}_x\text{Ge}_{20}\text{Se}_{80-x}$ system exhibits CTR at $x \approx 7$, while $\text{Pb}_x\text{In}_{25-x}\text{Se}_{75}$ system exhibits CTR at $x \approx 5$. We have measured the variation of thermal parameters as a function of composition in these systems, the results of which are discussed in chapter 4 of the thesis. The results are discussed in terms of the mechanism of CTR already outlined in chapter 3.

Chapter 5 deals with the photoconductivity measurements in Pb-Ge-Se and Pb-In-Se systems. It is found that the p to n transition gets reflected in these measurements. Temperature dependence of photoconductivity is also measured. The results obtained are analyzed in terms of the existing photoconductivity models, correlating them to the mechanism of p to n transition in these systems.

In chapter 6 we report the results of our electrical switching studies on $\text{In}_x\text{Te}_{100-x}$ ($x = 20-40$) glass system that exhibit CTR. We have also measured the variation in thermal parameters of the samples during electrical switching.

Thermal parameters of Ge-As-Se system are reported in chapter 7 of thesis. We have measured the thermal parameters as a function of the average coordination number Z . The effects of various topological thresholds on thermal parameters are discussed in this chapter.

Chapter 8 is the concluding chapter incorporating overall conclusions of the work presented in earlier chapters. Further scopes for the work that can be done in this direction on other chalcogenide glass systems are also discussed.

Most of the results presented in this thesis have either been published or communicated for publication in the form of following papers/symposium proceedings.

1. Carrier type reversal in Pb-Ge-Se glasses: photopyroelectric measurement of thermal conductivity and heat capacity
Applied Physics Letters **78** (2001) p. 745.
2. Photoconduction in Pb-Ge-Se semiconducting glasses exhibiting carrier type reversal
Indian Journal of Pure & Applied Physics **38** (2000) 827.
3. Photopyroelectric determination of thermal parameters across $p \rightarrow n$ transition in Pb doped Ge-Se glasses
Analytical Sciences **17** (2001) s99.
- 4 Thermal conductivity and heat capacity of certain chalcogenide glass systems exhibiting carrier type reversal (communicated).
- 5 Thermal properties across thresholds in Ge-As-Se glasses (communicated).
- 6 Thermal conductivity and heat capacity in In-Te glasses during electrical switching (communicated).

Symposium papers presented during the course of work

1. Photoconductivity properties around $p \rightarrow n$ transition in Pb-Ge-Se glasses
Proc. DAE Solid State Physics Symposium, Vol.42 (1999) p.293.
2. Photopyroelectric determination of thermal parameters across $p \rightarrow n$ transition in Pb doped Ge-Se glasses
Proc. XI International Conference on Photoacoustic and Photothermal Phenomena, Kyoto, Japan, June 25-29 (2000).

3. Carrier type reversal in Pb-In-Se glasses reflected in thermal transport measurements
Proc. DAE Solid State Physics Symposium, Bilaspur, Dec 27-31, (2000).
4. Photoconductivity across p to n transition in Pb-In-Se semiconducting glasses
National Seminar on Current Trends in Material Science, M. G. University, Kottayam, March 23-24 (2001).
5. Carrier type reversal in chalcogenide glasses: Some thermal facts and figures
National Seminar on Current Trends in Material Science, M. G. University, Kottayam, March 23-24 (2001).
6. Thermal properties across thresholds in Ge-As-Se glasses
DAE Solid State Physics Symposium, BARC, Mumbai, Dec 27-31 (2001)
(communicated).

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CHAPTER-1

Review of chalcogenide glasses

1.1 Introduction

A perfect crystal is a solid, in which the atoms or group of atoms are arranged in a pattern that repeats periodically in three dimensions to an infinite extent. An imperfect crystal is one, which possesses defects such as vacancies, interstitial foreign atoms or dislocations. Strictly speaking, most crystals are imperfect. On the other hand, non-crystalline or amorphous materials possess randomness or disorder in the arrangement of their atoms. Randomness or disorder can occur in several forms, of which topological (or geometrical), spin, substitutional and vibrational disorders are the most important. These types of disorders are illustrated in Fig. 1.1. Disorder is not a unique property. It must be compared with some standard, and that standard is the perfect crystal.

Topological disorder is that form of randomness in which there is no translational periodicity whatsoever (Fig. 1.1a). Certain amorphous materials have considerable short-range (or local) order, while others have little. However, both have no long-range order. So amorphous solids are therefore distinguished by their lack of periodicity and long-range translational order. This thesis deals with materials that possess topological disorder.

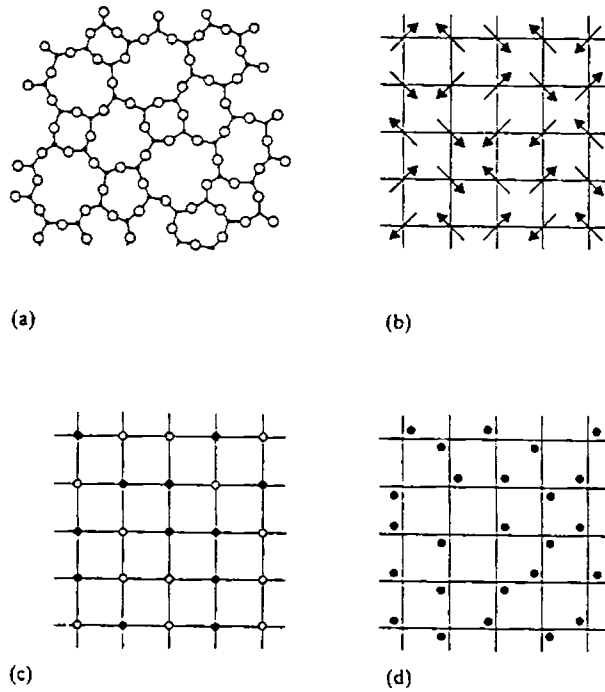


Fig. 1.1 Types of disorder

- (a) topological disorder (b) spin disorder
(c) substitutional disorder (d) vibrational disorder.

Another variety of randomness is spin or magnetic disorder, in which the underlying crystalline lattice is preserved, but each atomic site possesses a spin or magnetic moment oriented randomly (Fig. 1.1b). Materials possessing randomness in spin are called spin glasses. A further kind of randomness is substitutional disorder in which, although the underlying crystalline lattice is preserved, the material is in fact an alloy with one type of atom randomly substituting the other in the lattice (Fig. 1.1c). The final category of randomness is vibrational disorder of a crystalline lattice (Fig. 1.1d). The concept of a perfect crystal is only valid at absolute zero of temperature, and at any finite temperature, the random motion of atoms about their equilibrium positions destroys the perfect periodicity. However,

vibrational disorder is not another form of topological disorder, since although the atoms are vibrating, they do so about their equilibrium crystalline positions, which are not topologically disordered.

The terms amorphous and non-crystalline are synonymous and can be used interchangeably, whereas the term glass is more restricted. The definition of glass is that, it is an amorphous solid, which exhibits a glass transition, even though the term has conventionally been used for an amorphous solid prepared by quenching the melt. If the randomness in a liquid is frozen we get a solid, which is a glass. For a solid glass, the shear viscosity exceeds $10^{14.4}$ poise.

1.1.1 The glass transition

Materials that can be quenched from a melt to form an amorphous solid are represented by all the major types of bonding interactions found in solids viz., covalent, ionic, metallic, van der Waals' and hydrogen bonds. Consequently, they can be insulating, semiconducting or metallic in nature.

When a vapour is cooled, it forms a liquid and when the liquid is cooled further it solidifies. A liquid may solidify in the following two ways, (i) discontinuously to a crystalline solid or (ii) continuously to an amorphous solid. These are shown in Fig. 1.2. This figure should be read from right to left, since time runs in that direction during the course of temperature lowering. A sharp break or bend in $V(T)$ marks a change of phase occurring with decrease of temperature. The first occurs when the gas condenses to the liquid phase at the boiling temperature T_b . Continued cooling decreases the liquid volume in a continued fashion, the slope of the smooth $V(T)$ curve defining the liquid's volume coefficient of thermal expansion. Eventually, when the temperature is brought low enough, a liquid \rightarrow solid

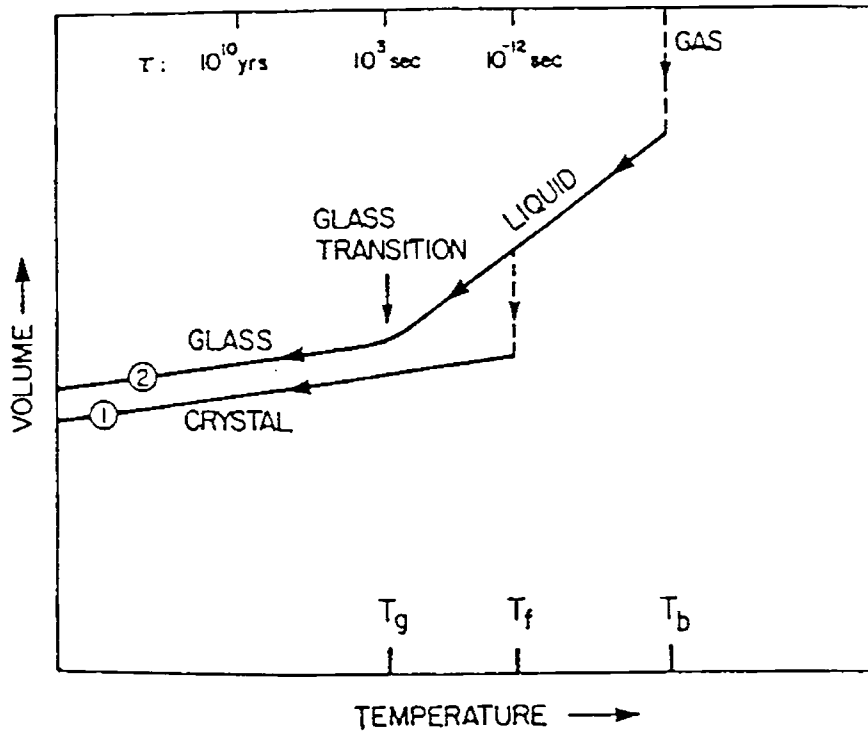


Fig. 1.2 The two general cooling paths by which an assembly of atoms can condense into the solid state. Route (1) is the path to the crystalline state. Route (2) is the rapid quench path to the amorphous solid state.

transition takes place following any one of the two ways cited above and as indicated in Fig. 1.2.

The liquid \rightarrow crystal transition is marked by a discontinuity in $V(T)$, an abrupt contraction to the volume of the crystalline solid at temperature T_f . This is usually the route taken to arrive at the solid state if the quenching experiment is carried out at a sufficiently low cooling rate. But at sufficiently high cooling rates, it is found that most materials alter their behaviour and follow route (2) to the solid phase. Temperature T_f is bypassed and the liquid phase persists until a lower temperature T_g is reached. The liquid \rightarrow glass transition occurs in a narrow temperature interval near T_g , the glass transition temperature. There is no volume

discontinuity as such; instead $V(T)$ bends over to acquire a small slope characteristic of the low thermal expansion of a solid.

Experiments show that the observed glass transition temperature T_g depends upon the cooling rate at which the experiment is carried out. This dependence is very small in most solids. Typically, changing the cooling rate by an order of magnitude causes T_g to shift by a few degrees Kelvin. The reason that T_g shifts to lower temperatures when the cooling process is extended over longer times resides in the temperature dependence of a typical molecular relaxation time τ . The quantity $1/\tau$ characterizes the rate at which the molecular configuration (atomic scale structure) of the condensed system adapts itself to a change in temperature. This quantity varies enormously during the cooling process as indicated in Fig. 1.2. As soon as the temperature of the liquid is lowered to T_f , it may take route (1) to the solid state and crystallize. But crystallization takes time. Crystalline centres must form by nucleation and then grow by outward propagation of the crystal / liquid interfaces. With the liquid being cooled at a finite rate, the liquid may be taken below T_f along the $V(T)$ trajectory, which smoothly continues the curve from higher temperatures. In the temperature interval between T_f and T_g , the liquid is referred to as supercooled liquid. If its temperature can be taken below T_g before crystallization has had time to occur, the liquid solidifies as the glass and remains in this form essentially indefinitely. Therefore, glass formation is a matter of bypassing crystallization.

The thermodynamic variables, volume, entropy and enthalpy are continuous through glass transition, but exhibit a change of slope there. This implies that at T_g , there should be a discontinuity in derivative variables such as coefficient of thermal

expansion, compressibility and heat capacity. This is indeed the case in all glasses. Even though a number of theories have been put forward to explain glass transition, it still remains a phenomenon, which is not yet completely understood.

1.2 Preparation and classification of amorphous solids

1.2.1 Preparation

The glass forming ability of solids vary considerably, but, in principle, all solids can be prepared in the amorphous state, provided the required necessary physical conditions are satisfied. Nearly all materials can, if cooled fast enough and far enough, be prepared as amorphous solids. Thus, the essential ingredient in the preparation of an amorphous solid is speed and the formation of amorphous state is a process of bypassing crystallization [1]. Usually cooling rates of 10^2 - 10^6 K sec⁻¹ are required to freeze the disorder. For pure metals, cooling rates of 10^9 K sec⁻¹ are required. Details of glass formation and related processes are discussed in many review articles [2-6].

There exists a number of ways for the preparation of materials in the amorphous state. Thermal evaporation, sputtering, chemical vapour deposition and melt quenching are the most commonly used techniques to prepare amorphous materials [7]. Amorphous thin films are usually prepared by vapour deposition or sputtering. Bulk glasses having a well-defined T_g are usually prepared by the melt quenching technique.

1.2.2 Classification

As already stated, amorphous solids are characterized by different kinds of bonding, and consequently they can be insulating, semiconducting or metallic in nature. Amorphous semiconductors can, in general, be divided into two groups as tetrahedrally coordinated silicon type materials and two-fold coordinated chalcogenide glasses [8]. Chalcogenide glasses contain one or more of the chalcogen elements, sulphur, selenium or tellurium of the sixth group of the periodic table. The distinction between these two classes can be well accounted for on the basis of chemical considerations. The four-fold coordination in Si leads to symmetrical bonding and the formation of rigid structures. In this case a continuous random network with tetrahedral bonds can be constructed with negligible density deficit and very little possibility for local reorganization of atoms. On the other hand, the two-fold coordination in chalcogens is highly asymmetrical and the structure gives rise to greater degree of flexibility. A major distinction comes from the fact that, in chalcogens, but not in Si, the valence band is formed from non-bonding lone pair p electrons and is very important when we consider the defect chemistry and various properties of chalcogenide glasses that differentiate it from Si type materials.

Out of these two classes of materials, chalcogenide glasses can be prepared in the bulk, as well as thin film forms, but a direct comparison of the properties of thin film and bulk glasses may not be possible. However, Si type materials cannot often be prepared in the bulk form by the melt quenching technique. These materials are usually prepared in the thin film form. The reason why certain materials can be prepared in the thin film as well as bulk forms, while others can only be prepared in the thin film form can be explained by the nature of chemical bonds present in these

materials. This difference has its origin in the mismatch between constraints and the number of degrees of freedom in three dimensions and the flexibility required to accommodate the mismatch. The flexibility of covalent bond angles is largest for the two-fold coordinated Se type materials and least for the tetrahedrally coordinated Si type materials. The reason for this is the greater variety of admixture from other atomic orbitals to the covalent bond when the coordination number is less than the number of valence electrons. Therefore, based on chemical considerations and the average coordination number Z , a classification of amorphous solids can be made as shown in Fig. 1.3. According to this, glasses are restricted to $3 \geq Z \geq 2$, and materials with higher connectivity, i.e., $4 \geq Z \geq 3$ are over constrained amorphous, while those with $Z < 2$ are under constrained amorphous. The average coordination number $Z = 4$ separates non-crystalline metals from semiconductors or insulators.

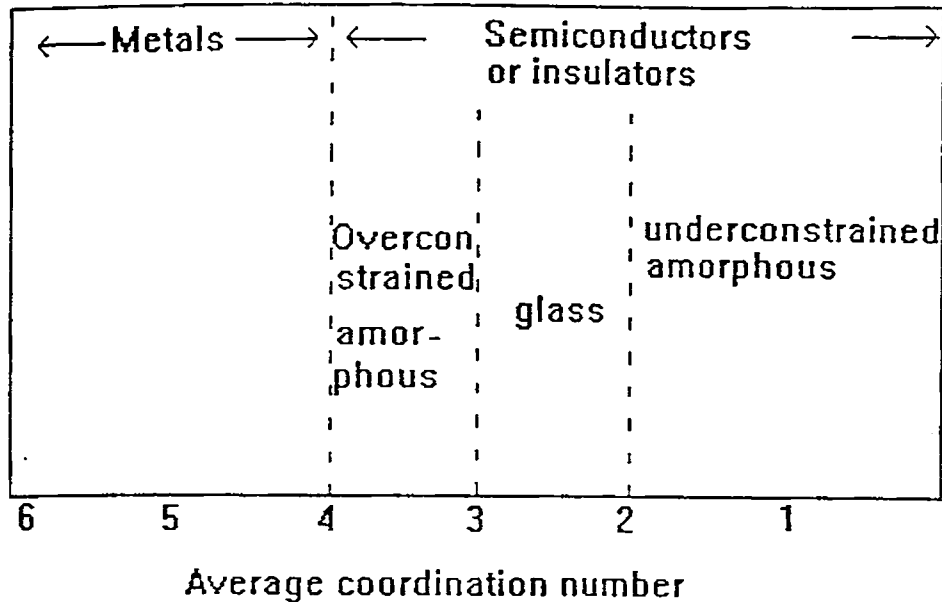


Fig. 1.3 Classification of non-crystalline solids based on the average coordination number.

1.3 Structural properties

Even though amorphous materials lack long-range periodicity of constituent atoms, the disorder is not complete on the atomic scale [9]. Short-range order similar to that present in crystalline materials is also present in these disordered materials. In chalcogenide glasses, the covalently bonded atoms are arranged in an open network with order extending up to 3rd or 4th nearest neighbours and they are also referred to as network glasses [10]. The semiconducting nature of chalcogenide glasses is however, a direct consequence of the covalent bonding that exists in these materials.

The structure of an amorphous solid can never be determined unambiguously. The absence of periodicity in a glass makes the unit cell concept invalid or one can consider unit cell is infinite which implies that the coordinate of each and every atom should be known. The uncertainty in the structure of an amorphous solid is compounded by the fact that the structure of a non-crystalline material, at both microscopic and macroscopic levels, often depends on the details of method of preparation. Furthermore, in general, more than one experimental structural probe must be used to obtain as complete a picture as possible of the structural arrangement in an amorphous solid. The best information one can get from the diffraction methods for a glass is the radial distribution function (RDF), which expresses the probability of finding another atom at a given distance from an arbitrary point.

In both amorphous and crystalline materials, the chemical forces holding the atoms together are the same. Therefore the amorphous state is always defined with reference to a crystalline state [7, 11]. From a comparison of radial distribution functions of amorphous and crystalline films of silicon, it has been revealed that

covalent glasses exhibit some ordering in their atomic structure. The structural ordering in covalent glasses can be classified into two types depending on their length scale [12, 13]. They are of short-range order in the range 2-5 Å and of medium-range order in the range 5-20 Å.

Since there is no unique structure for an amorphous material, structural modeling is very useful in determining the structure of amorphous solids. The structure of amorphous semiconductors is developed by the repetition of one or more basic molecular units in a way that cannot be identified topologically with any known crystalline structure or with any periodic array. The atomic order within a molecular unit might be similar within small bond angle distortions in both crystalline and amorphous phases. This reveals the importance of short-range order in describing the structural behaviour of a non-periodic network. The most important aspects of the short-range order are the number and type of immediate neighbours, and their spatial arrangement about a given reference atom. Given the short-range order, with three parameters viz., the number of bonds, the bond length and the bond angle having well defined values in a narrow range, it is possible to construct a model for the amorphous structure. Such models are known as random network models. The continuous random network (CRN) model, the first model of an ideal glass proposed by Zachariasen [14] is the basis for all structural models. A number of structural models have been proposed to explain the various structure related properties of amorphous materials.

1.4 Structural models of amorphous solids

1.4.1. Network models

Covalent random network (CRN) model proposed by Zachariasen is more applicable for covalent glasses. He imposed some rules to be followed while building the model, based on the local similarity between crystalline and amorphous materials. A definite short-range order is imposed as each atom fulfills its chemical valence requirements according to Mott's $(8-n)$ rule [15], where n is the number of valence electrons of the particular atom. The underlying principle of this model is that a closed outer shell of eight electrons is the most stable structure. Small variations introduced in bond lengths and bond angles lead to disorder in the glassy matrix. The variation in bond length is much less and they are within 1 % to those found in crystals. The major source of randomness comes from the variation in bond angles. The flexibility of covalent bond angles is largest for the two-fold coordinated chalcogens and least for tetrahedrally coordinated group IV elements. CRN model generates amorphous structure without taking into account structural defects such as dangling bonds and voids and it is not adequate to account for features observed in medium-range order.

The structure of chalcogenide glasses can be more appropriately described by the random covalent network (RCN) model or chemically ordered covalent network (COCN) model [16, 9].

Chalcogenide glasses can be prepared over a wide range of compositions. This means that glasses with non-stoichiometric compositions can also be prepared which will contain bonds between like atoms. It is essential to estimate the fraction

