CHAPTER ONE
CHAPTER - ONE
AMORPHOUS SEMICONDUCTORS

1.1 An Introduction:

The science and technology of materials are constantly undergoing vital changes. We have now entered into an age of materials science where-in materials go by a variety of interpretive names such as smart, intelligent, high performance, hi-tech, tailored, engineered etc. The suitability of the materials for high technology applications requires additional information about the material in respect of optical, structural and electrical characterization. Characterization of materials from optical, structural and electrical consideration involves the determination of features such as optical band gap, nature of band gap, crystallographic structure, chemical composition and current voltage characteristics of the materials. The information about these features is significant for the reproduction of materials.

Semiconductors are the basic components of the integrated circuits and are responsible for the starting rapid growth of the electronics industry in the past fifty-to-sixty years worldwide. Because there is a continuing need for the faster and more complex systems for the information era, existing semiconductors
are being studied for improvement, and new ones are being invented. Whether it is for higher speed, lower power, higher density, higher efficiency, or new functionality, the number and types of semiconductors have been growing steadily in the fascinating field.

It is difficult to have a clear quantitative definition of semiconductor. Based on conductivity, materials can be classified into three groups: (i) metal (ii) semiconductor, and (iii) insulator. It is to be noted that the most important feature of the semiconductor is that it can be doped with impurities to different concentration levels, so ever semiconductor material can cover a range of conductivity.

The earliest device, not necessarily made of semiconductor material, is probably the resistor, implied by Ohm’s law back in 1826. Vacuum tubes started around 1904, and were the major electronic components in the early radio era through World War II. The real world of the semiconductors was in 1947 with the invention of the bipolar transistor.

According to their properties and behavior, Materials can be classified as crystalline and non-crystalline solids. In a crystal, the atoms are arranged in a periodic repeated pattern, whereas no such regularity occurs in non-crystalline material. Again crystalline solid can be divided into two as single crystal, where entire solid consists of only one crystal and polycrystalline, where the solid has an aggregate of many crystal separated by well defined boundaries.
Optical properties of amorphous and crystalline semiconductors are of special interest. Recent years have seen an upsurge in interest in the electronic properties of non-crystalline materials. These lack the simple structures and long range order that make crystals relatively easy to understand. The interest, both at Sheffield and worldwide have largely concentrated on amorphous silicon and its relatives. A wide variety of measurements have made along with the photoluminescence methods, for a broad understanding of the semiconductors. These materials are widely used in Xerox copiers, photovoltaic cells and large area displays.

The marvels of modern semiconductor technology follow from sound physical knowledge and metallurgical control of single crystal materials. While semiconductor phenomena are not unique to crystals, active devices almost always involve single crystals. Amorphous semiconductors, with the well-established crystalline foundations as a departure point, offer new frontiers for research and, hopefully, promise for technological developments.

The fundamental properties of the semiconductors mainly depend upon the energy band structure for their operation [1,2]. Every semiconductor consists of a forbidden energy gap in which no energy levels can exist and above & below the energy gap there exist two energy bands. The upper band is known as conduction band while the lower band is known as valance band. The difference
between these two bands is known as energy band gap $E_g$ a quite important factor for semiconductors.

The classification of semiconductor depends upon the corresponding positions of conduction band and valance band in K-space (Fig. 1.1). When the conduction band minimum and the valance band maximum are located at the same K (wave vector) value = 0 then this type is known as direct band gap semiconductors. In this case there will be no change in momentum of photon in the transition from valance band to conduction band. Almost all the semiconductors of the group II - VI are direct band gap type semiconductors. But if there are a difference in the K-values of valance and conduction band then these are indirect band gap semiconductors. Any transition from valance band to the conduction band for different K-values involves a photon of light momentum. Some examples of indirect band gap semiconductors are Si, Ge, Al etc. The fact of direct and indirect band gap is a deciding factor for devices.

The absorption spectra, reflection spectra and transmission spectra of the sample films will help us to study the optical, structural and electrical properties of these films. Characterization of materials from optical, structural and electrical consideration involves the determination of features such as optical band gap, nature of band gap, crystallographic structure, chemical composition and current voltage characteristics of the materials. The information about these features is significant for the reproduction of materials.
Indirect band gap in Diamond

Direct band gap in Zinc Blende

Direct band gap in Wurtzite

Conduction band

Fermi level

p-region

n-region

Barrier region
1.2 Semiconductor Junctions:

When a p-type semiconductor is contacted with n type semiconductor, electrons from n side of the contact diffuse into p side due to large number of electrons in n side. In p region, they recombine with free holes. As this process goes on, p region becomes negatively charged and n region positively charged. A dynamic equilibrium exists when a potential differences stops the further motion of the majority charge carriers. A space charge is created in n and p regions both. The Fermi levels of n and p-type semiconductors become equal at the equilibrium. Fig. 1.2 shows the energy band diagram of a p–n junction.

When n type semiconductor is contacted with a metal having higher work function than that of semiconductor, the electrons which come due to ionization of donor levels, flow into the metal until the Fermi levels of metal and semiconductor become equal. In this process, the surface of the semiconductor becomes positively charged due to depletion of electrons.

The contact of p-type semiconductor with a metal having lower work function than that of semiconductor also makes a barrier where a negative space charge region is created in the semiconductor, which stops the flow of holes. Fig. 1.3 shows the energy band diagram of such a barrier, which is also known as schottky barrier.
Figure 1.3a Energy band diagram of a Schottky barrier using p type semiconductor.

Figure 1.3b Energy band diagram of a Schottky barrier using n type semiconductor.
1.3 Hall Effect In Semiconductors:

When a magnetic field is applied at right angles to a conductor carrying a current, a voltage is developed across the metal in a direction perpendicular to the direction of current and magnetic field both. This phenomenon known as Hall effect has been observed in semiconductor.

Also, in n-type semiconductor, electrons are the majority charge carriers so hall coefficient is negative. On the other hand, in p type semiconductor, holes are the majority carriers and Hall coefficient is said to be positive. In intrinsic semiconductor, Hall coefficient is very small. Hall voltage in these semiconductors is only due to different mobility of electrons and holes.

In general, for crystalline semiconductor, the sign of the Hall voltage is used to determine whether a semiconductor is p-type, n-type or the sign of Hall coefficient is opposite to what is expected from the nature of the majority charge carriers.

1.4 Crystalline Semiconductors and their properties:

Crystalline semiconductors are known for a long time and the theory of these semiconductors is also well established using the concepts of long range order in crystals. Since the generation of charge carriers can be controlled by temperature, light, high fields and impurities, semiconductors are most suitable for various kinds of solid-state devices. The crystalline semiconductors are being used in making p–n junction diodes, schottky diodes, transistors, thyristers, field effects
transistors, photodiodes, solar cells, high-energy particles detectors and many more devices. Many works [3-5] have discussed the details of these devices.

By semiconductor we mean a substance, which has conductivity in between that of a conductor and an insulator. The distinction between an insulator and semiconductor is difficult to draw. However, normally a substance having conductivity less than $10^{-14}$ ohm$^{-1}$ cm$^{-1}$ does not fall under the category of semiconductor. The distinction between metal and semiconductor is quite sharp not by the conductivity range but by the temperature coefficient of resistivity which is positive in case of metals and negative for semiconductors.

At absolute zero of temperature, the valence band of a semiconductor is completely filled and conduction band is completely empty. Due to thermal energy at any temperature other than absolute zero, a number of electrons become free. In terms of bands, one can say that electrons are excited to the conduction band and contribute to the conductivity. The empty state left in the valence band is known as a hole, which can also contribute to the conduction process. The conductivity of a semiconductor therefore has two components as follows:

$$\sigma = n e \mu_n + p e \mu_p$$  \hspace{1cm} (1.1)

Where $n$ and $p$ are the density of electrons and holes respectively $\mu_p$ and $\mu_n$ are their respective mobilities.
It must be noted that the donor and acceptor states in a semiconductor are localized in space because the impurity atoms occupy certain atomic sites in the structure. Because of this, donor and acceptor states are frequently called localized states.

In addition to donor or acceptor states, other kinds of defects in semiconducting crystals can also be produced. Each type of defects has a definite energy and produced localized states at that energy. These localized states can act as traps for electrons or holes. When probability of capturing electrons and holes become equal, a localized state can act as a recombination center.

Generation and recombination of charge carriers are simultaneous in a semiconductor. In thermal equilibrium, equal number of like charges appears and vanishes per unit time. The conductivity of a semiconductor depends upon these equilibrium electron and hole densities.

The quantum statistic plays an important role in determining the number of electrons and holes in conduction and valence band respectively.

A systematic calculations show that the conductivity in intrinsic semiconductors is given by

$$\sigma \propto \exp \left[ \frac{E_C - E_F}{kT} \right]$$

(1.2)

Where $k$ is the Boltzman's constant, $E_C$ is the energy at the bottom of the conduction band and $E_F$ is known as the Fermi energy. At the absolute zero
of temperature, \( f(E) = 1 \) for \( E < E_f \) and \( f(E) = 0 \) for \( E > E_f \) is the probability of a quantum state, at energy \( E \), to be occupied by electron.

For semiconductor \( E_f \) lies almost in the middle of the band gap, i.e.,

\[
E_f = \frac{E_C - E_V}{2}.
\]

Here, \( E_V \) is the energy at the top of the conduction band. The conductivity can therefore be written as

\[
\sigma \propto \exp \left( \frac{-E_C - E_V}{2kT} \right)
\]

Equation (1.3) shows that the \( \text{s vs} \frac{1}{T} \) curve should be a straight line for an intrinsic semiconductor. The slope of this curve can be used to calculate the band gap \( E_g \) (\( E_C - E_V \)).

1.5 Concept of Amorphous Semiconductors:

In the early nineteenth century, solids were known as amorphous if they had a formless fracture surface. With the discovery of x-ray and electron diffraction, it was found that the substances, which were amorphous by fractography, were also non-crystalline. Since then, the word amorphous is used to mean non-crystalline on any significant scale. Long range order (periodicity of atoms for a larger distance) is almost absent in amorphous materials. However, they may have short range order up to a few atomic distances.

The amorphous threshold switch, named after the inventor S. R. Ovshinsky whose landmark paper in 1968 sparked a new field of research in the
Thesis of Mala Shukla

1970's and 1980's [6]. In 1950's, it was found that non-crystalline solids and liquids, which do not have periodic structure, could also behave as a semiconductor. A. F. Loffe and A. R. Regal suggested that electronic properties of these semiconductors originate from short-range order rather than long range order.[7]

The improved understanding of the amorphous state which came from these studies has revived and refreshed interest in traditional glasses, particularly those doped with rare earth transition metals, which have optoelectronic applications in, for example, fibre optical amplifiers, as well as for coloured glasses. Organic is another research area which benefits from the insights gained from disordered materials.

Amorphous substances are prepared by rapid cooling of the melt and thin film by condensing vapours on a substrate. In both the cases, due to rapid cooling, some of the bonds are not formed. These broken bonds are known as dangling bonds. A part from the dangling bonds, some other kind of defects can also be created during the preparation of thin films. The properties of amorphous substances, therefore, depend strongly on preparation condition and results differ from one laboratory to other laboratory. It is very difficult to draw any conclusion unless a lot of experimental data is available. The properties of glasses are relatively more reproducible in the thin films.
Amorphous substances pose great problems to theoretical physicists also as the mathematical simplicity of the periodic structure does not exist in these materials. In these cases, the mathematics becomes so complex that it is very difficult to draw any conclusion from the calculations. This is the reason why our knowledge is poor in case of amorphous substances as compared to crystals. The mankind knows the fact of transparency for the last 10,000 years but the theoretical explanation of this transparency does not yet exist in the scientific literature.

Amorphous substances do not show sharp lines in bragg diffraction pattern unlike crystalline substances. A hole is generally observed in these materials. Amorphous semiconductors do not have long range ordering of their constituent atoms. The array of equilibrium atomic positions is strongly disordered. It was long believed that the amorphous materials couldn’t behave as semiconductors. B. T. Kolomicts is the first person who started working on glasses containing one or more chalcogenide element (S, Se and Te)[1]. These glasses have larger properties, instead of conventional sixth group element, which was used to prepare glasses. It was found that these glasses behave similar to intensive crystal semiconductor. It was believed that these semiconductor are of no use because these semiconductor could not be constructed like n or p-type semiconductor by doping with V and VI group elements of the periodic table. Therefore one can classify the semiconductors only in two categories i.e.
crystalline and non-crystalline. Chalcogenide glass, is the another name of non-crystalline semiconductors.

For an amorphous solid, essential aspect with which its structure differ with respect to that of crystalline solid is the absence of long range order. There is no translation periodicity. The lack of long-range order in glasses implies randomness at large separations; the atomic-scale structure is highly nonrandom for a few interatomic distances about any given atom. Short-range order is very much in evidence in the structure of amorphous solids. Non crystalline solids made by non-conventional methods such as vapor deposition Sol-gel and solid state amorphization processes are sometimes referred to as glass and other times as amorphous solids. The lack of long-range order makes these materials very hard to extract structural information from the diffraction experiments. Many important amorphous solids are representable by disconnected covalent graph that is they are molecular solids.

For a long time it was thought that only a relatively restricted number of materials could be prepared in the form amorphous solids, and it was common to refer to these "special" substances (e.g. oxide glasses and organic polymers) as "glass forming solids". This notation was wrong and it is now realised that "glass forming ability" is almost a universal property of condensable matter. B. T. Kolomiets and his associates in the USSR first tried other VI group elements (S. Se. and Te) in place of conventional element 'O' which was used to
prepare oxide glasses. They found that glasses prepared using one or more chalcogen elements (S, Se and Te) showed the semiconducting properties. Most of the chalcogenide glasses materials contain one or more of the chalcogen elements of the VI column of the periodic table. An extensive research on amorphous semiconductors started when S. R. Ovshinsky detailing the various types of switching phenomena that characterized a large class amorphous solid, and the subsequent publicity describing many potential applications for these phenomena [6]. He also demonstrated the use of chalcogenide thin films for computer memory. A further interest in these semiconductors arose when W.E. Spear and P.G. LeComber at the University of Dundee, U.K. 1975, developed a technology to produce n and p-type amorphous silicon similar to their crystalline counterpart [8]. Since then, this material is being utilized in various solid state devices.

In many amorphous materials it is possible to control the short-range order parameter. The short-range structure can be made quite different from that in crystalline state of that substance. The structures therefore become a new variable by which the properties can be changed drastically in amorphous materials.

The preparation of amorphous substance is, much easier than growing single crystals. This feature of amorphous materials makes them suitable for making devices for commercial purposes at a cheaper rate than crystalline ones. A large number of defects are introduced in crystalline substances when they are irradiated with high-energy particles. The properties of the crystalline
substances thus change drastically after irradiation. On the other hand, amorphous substances do not have such drastic changes as they are already in disordered state. This feature of amorphous substances makes them suitable for space applications.

Long range order is almost absent in amorphous semiconductor, though they can have short range order up to a few atomic dimensions. The most important elements, which preserve short-range character, are silicon and germanium from group IV, arsenic, antimony and bismuth from group V and sulfur, selenium and tellurium from group VI of the periodic table. Elements from other groups may also be present but usually as a minority constituent.

Amorphous semiconductors may be single elements such as bulk selenium, tellurium or thin films of silicon and germanium; they may be compounds such as arsenic tritelluride; or they may be multicomponent alloys that form bulk glasses over a broad range of compositions.

Amorphous substance, unlike crystalline ones, does not have a sharp melting point. The transition from solid state to liquid state takes place within a finite time interval known as softening time.

Amorphous substances are isotropic, i.e. the properties do not depend upon the direction of measurement. Crystals are well known for their an isotropic nature where properties in different directions differ considerably.
Unlike crystalline substances, amorphous substances can exist in metastable structural states. New compositions and mixtures can therefore be prepared which may exceed the limits of thermodynamic equilibrium.

1.6 Properties and Technological Importance of Amorphous Semiconductors:

At early stages, it has long been believed that the chalcogenide glasses show the p-type conduction only and that the control of the conduction type is impossible by doping technique since the valence of doped atoms is always satisfied in the glasses. According to the band model of amorphous semiconductors, developed by Mott et. al. [9,10] and Kastner et. al. [11] the above situation is explained by the pinning of Fermi energy due to the equilibrium between negatively $D$ and positively, $D'$charged dangling bonds.

Considering electricity, metals are good conductors while non-metals are insulators. The materials, having conductivity in between $10^{-6}$–$10^{4} \text{ } \Omega^{-1}\text{ }\text{cm}^{-1}$ are metals, $<10^{-6} \text{ } \Omega^{-1}\text{ }\text{cm}^{-1}$ are insulators $10^{4}$ – $10^{-10} \text{ } \Omega^{-1}\text{ }\text{cm}^{-1}$ are semiconductors. Metals have positive temperature coefficient of resistance while semiconductors have negative temperature coefficient of resistance. Semiconductors are very much sensitive to the presence of light and the variation of temperature. Semiconductors may be characterized by their structure, energy effective mass and carrier mobility. The properties may be altered by impurity doping [12, 13].
Those solids, which are out of long range order or crystallinity is known as amorphous. The properties of amorphous solids depend upon the preparation techniques. Except some examples these are unstable in reference of crystalline materials. Silicon and Germanium are of diamond structure, the II-VI group materials are of complicated structure due to the tendency of these to crystallize in a various polymorphic modification: II-VI compounds are either of zinblende structure or of hexagonal structure [14, 15].

Optical properties of the material may help to understand the band structure of the substances. [16-18]. When a light beam is incident on any semiconductor material, some part of the beam undergoes reflection, some passes through (transmission) and the material absorbs rest part. The interaction between photons and electrons takes place as same as between photons and the crystal lattice.

The photons having energy \( \hbar \nu (\hbar \nu > E_g) \) there exists inter band optical transitions but photons of energy \( \hbar \nu (\hbar \nu > E_g) \) excitation transitions or the transitions between bands and doping levels can exists.

A lot of research work is being carried out on in the area of amorphous and liquid semiconductors and there is a hope that very soon these semiconductors will overtake their crystalline counterpart.
1.7. DC And AC Conductivity:

A dc and ac conductivity vary from sample to sample and results are sometimes highly intriguing. However, generally it is observed that dc conductivity ($\sigma_{dc}$) increases with temperature, similar to intrinsic crystalline semiconductors, in high temperature region (150 k and above). Single activation energy has been observed from the slope of $\ln \sigma_{dc}$ vs $1/T$ curve in the above temperature range.

At lower temperatures (below 150 k) $\sigma_{dc}$ shows variable range hopping type conduction as suggested by Mott and Davis [19] considering the localized states near Fermi level. According to these authors, $\sigma_{dc}$ due to this process is given by

$$\sigma_{dc} \propto \exp \left[ - \frac{T_0}{T} \right]$$

Where $T_0$ depends upon the density of localized states near Fermi level. This type of conduction is observed in various types of amorphous semiconductors. However, the chalcogenide glasses do not show this type of conduction. The reason of this discrepancy has been associated with the paired defect states in chalcogenide glasses. Unlike other amorphous semiconductors they do not have unpaired electron states.
AC conductivity is observed in amorphous semiconductors including chalcogenide glasses. AC conductivity \( (\sigma_{ac}) \) shows almost linear variation with angular frequency \( (\omega) \). One therefore writes

\[
\sigma_{ac} \propto \omega^s 
\]

...............(1.5)

Where \( s \) is found to have values from 0.8 to 1.0 for various amorphous semiconductors. AC conductivity is found weakly temperature dependent at low temperatures. At very high frequencies in low temperature range, \( \sigma_{ac} \) which is explained due to contact effects.

In amorphous semiconductors also, \( \sigma_{ac} \) is explained assuming the hopping conduction in localized states in the band tails and/or near Fermi level.

1.8 Optical Absorption:

Similar to crystalline semiconductors, optical absorption edge is observed in amorphous semiconductors also. The edge is, of course, not very sharp due to the localized states present in the band gap. These localized states near the band edge arise due to the absence of long-range order in these semiconductors.

1.9 Mobility:

Mobility of electrons and holes in amorphous semiconductor is much less as compared to crystalline semiconductors. This is expected in these semiconductors as they do not have the periodicity of crystals. Due to small
mobility of charge carriers, the resistivity of these semiconductors is much larger as compared to their crystalline counterpart.

1.10 Hall Effect And Thermoelectric Power:

In amorphous semiconductors, the sign of the hall effect is always opposite to that obtained from thermoelectric power: An typed doped samples show a positive Hall coefficient and p type doped samples a negative one. On crystallisation, the Hall coefficient has the sign of the carrier. This discrepancy is explained by assuming the dominant transport due to hopping in localized states. In hopping conduction, the sign of the transfer integral and the number of sites necessary to make a closed path. The Hall voltage, therefore, may be positive even when electrons are the majority carriers.

1.11 Electron Spin Resonance:

Amorphous semiconductors show electron spin resonance (ESR) indicating the presence of free spins. This is probably because of dangling bonds, which are more likely in amorphous films. In case of thin films, not enough time for bonding is available before condensing on the cold substrate from vapour phase. Chalcogenide glasses do not show electron spin resonance under ordinary conditions. It is due to the presence of paired defect states which is quite favourable in these glasses as compared to unpaired defects.
1.12 Paramagnetic Behaviour:

Amorphous semiconductors, show paramagnetic behaviour due to the presence of free spins because of dangling bonds. However, as expected, paramagnetic behaviour is not observed in chalcogenide glasses.

1.13 Doping:

In the beginning, amorphous semiconductors could not be doped. It was thought that impurity atoms could satisfy their valence requirement by adjusting the nearest neighbour distance in an amorphous semiconductor. However, in 1975, Spear and Lecomber [8] could dope amorphous silicon, which was prepared by, glow discharge of silane gas. These workers also measured density of localized states in the gap by field effect technique and found that this density near Fermi level was three to four orders of magnitude smaller in these materials as compared to evaporated silicon. The question why amorphous silicon prepared by glow discharge of silane gas gives different properties than evaporated/ sputtered amorphous silicon was answered when Fritzsche et.al.[20] showed that these films contain hydrogen up to 10 atomic percent. On heating, hydrogen comes out of the films at round 400°C and then these films are as bad as prepared by evaporation or sputtering. Using I–R spectroscopy, it was found that in good quality films prepared at 300°C, hydrogen is attached to silicon as monohydride (see fig. 1.4).
Figure 1.4

- Curve a: T_s = 300K
- Curve b: T_s = 580K
- Peak 1: Si-H_2 Stretching
- Peak 2: Si-H_2 Stretching
- Peak 3: Si-O-Si
- Peak 4: Si-H_2 Bending
- Peak 5: (Si-H_2)_n
- Peak 6: Wagging
The fig.1.4 shows that hydrogen helps in removing the dangling bonds inside the materials and thus reducing the density of localized states near Fermi level. Since these films contain a large amount of hydrogen, hydrogenated amorphous silicon is known as an alloy of silicon and hydrogen (a-Si : H). This materials is alternatively produced by sputtering silicon in the presence of hydrogen [21]. Post hydrogenation of sputtered amorphous silicon also gives similar properties [22]. Recently, ion beam sputtering [23] and homogeneous chemical vapour deposition [24] have also been used to produced good quality a-Si : H films.

Hydrogenation of amorphous silicon films helps in the reduction of the density of localized states near Fermi level. This is the reason why these materials could be doped n or p-type.

Hydrogenation of chalcogenide glasses was also tried by H. Fritzsche and his co-workers [20] but the success could not be achieved in reducing the number of localized states and hence doping could not be achieved. S.R. Ovshinsky [24], however could change the conductivity of these glasses by 10 orders of magnitude by chemical modification of a particular glass. This modification was achieved by sputtering the materials at low temperatures. If one mix the same amount of impurity in the liquid phase the significant change in conductivity could not be achieved.
It has been reported [25] that p type Ge – Se – Bi glass transforms to n - type if Bi percentage is changed to more than 7 atomic percent. This opens a possibility of changing the density of localized states in the gap even by mixing the impurities in the liquid phase. Efforts are being made to prepare new compositions where p to n type changes could be made very sharp.

1.14 Switching:

Amorphous semiconductors show reversible switching in which sample goes from high resistance state (OFF State) to very small resistance state (ON State) when voltage applied across them exceeds a particular value called threshold voltage. Two types of switching are observed in these semiconductors, namely, threshold and memory. In threshold switching, sample comes back in its original state when current is reduced to a value less than the holding current. On the other hand, in the case of a memory switch, the system remains in the ON state when the current reduces to zero or is reversed. A memory switch, however, can be made to come back in its original state (OFF State) after applying a high current pulse for a short time. The memory switch retains its on states only if it is kept in that state for a certain period of time called lock on time. If sufficient time is not provided, a memory switch also behaves as a threshold switch. This lock on time is of the order of $10^{-6}$ sec.

The threshold voltage is found to depend upon temperature and receptivity of the materials independent of the type of switching displayed by
these materials. The power required for switching is also found to be the same for various types of materials having threshold and memory switching [20]. These results show that thermal effects are important in switching phenomena. The temperature near the electrodes is also observed to be quite high at the time of switching.

Two main models have been suggested for the switching in amorphous semiconductors. In the thermal model, the physical process is joule heating, which raises the temperature inside the semiconductor. The resulting increase in conductivity allows more current flow. A new stationary state is established when the heat generated away from the current filament equals the Joule heat generated in that region. In the electronic model of switching the high current is assumed to be due to high field conducting in these semiconductors. It is not easy to distinguish which of the phenomena is responsible for switching. An electro thermal model is, therefore, considered more appropriate for switching where thermal and electronic effects are simultaneous. The only problem is to find out which one is predominant in a particular material.

It is normally agreed that in the samples having large conductivity where large heating is possible, thermal effects are more dominant. In thin films or in samples having small conductivity, electronic process are dominant.
1.15 Classifications of Amorphous Semiconductors:

It is difficult to classify amorphous semiconductors as they have a wide spectrum having different properties. However, amorphous semiconductors are most easily classified by the type of chemical bonding that is primarily responsible for cohesive energy of materials. Amorphous semiconductors can be classified by considering ionic, covalent, metallic, Van der Walls and hydrogen bonded materials. The effects of long-range disorder on the electronic properties of solids are quantitative rather than qualitative. Van der walls and hydrogen-bonded solids generally have low cohesive energies and thus low melting temperatures. Thus the field of amorphous semiconductor can be broken down into ionic and covalent materials. The ionic materials, which have studied most, are the halide and oxide glasses, particularly the transition metal oxide glasses. Recently, simpler amorphous solids, such as V₂O₅ and NiO, have been prepared by rf-sputtering techniques. Being primarily ionic, the composition of these materials cannot be made to vary over a wide range, and the pure materials have just positional disorder.

It will be convenient to further break the covalent amorphous semiconductors into two classes, by separating out the purely elemental materials. This group, which is perfectly covalently bonded of course includes Si, Ge, S, Te and Se among others elements. Since all atoms are necessarily the same, these materials possess only positional disorder. Thus, they are the simplest amorphous
semiconductors to investigate theoretically. The remaining covalent materials include such binary materials as $\text{As}_2\text{Se}_3$ and $\text{GeTe}$, as well as the multicomponent boride, arsenide and chalcogen glasses. Being primarily covalent, there is nothing magic about the chemical composition. $\text{As}_2\text{Se}_3$ nominally contains 40% As and 60% Se but there is no reason why we cannot make an alloy of say 45% As and 55% Se or any other proportion we desire. Since the material is amorphous, we are not tied to any crystalline structure, and thus defects dangling bonds and antistructure are not the problems. Similarly, we can combine As, Se, Ge and Te and can produce, for example, $\text{As}_{31}\text{Se}_{21}\text{Ge}_{30}\text{Te}_{18}$ which is a chalcogenide glass. The significance of this is that the covalent amorphous semiconductors always possess compositional as well as positional disorder. As we shall see, the profound effects of this point disorder on the electronic band structure, are responsible for the distinctive properties of these glasses, and justifies their separation from the class of elemental amorphous semiconductors.

As in crystalline solids, many mixed ionic covalent amorphous materials exist and these have to be analyzed carefully. The similarities in short-range order and bond length, between corresponding crystalline and amorphous solids implies that the atomic electro-negativity is independent of the nature of material. We can use these properties to estimate the average fractional iconicity of a given alloy.
The structure of all non-crystalline semiconductors lack long-range order and far way from a site seems to be randomly distributed but short-range does exist. The state of material may be regarded as a supercooled liquid. Chalcogenide glasses material heat to melt in the form of a liquid and at the same instant freeze the position of every atom by quenching. Even in this freezed position they retain short-range order and the position of nearest neighbour remains nearly same.

In binary non-crystalline semiconductors besides positional disorder, compositional disorder also exists. For example in non-crystalline Ge or Te the structure becomes such that there becomes equal probability of finding Ge or Te atoms at any position. This is compositional disorder and exists in other binary non-crystalline semiconductors like As$_2$S$_3$ and others.

In multi-component non-crystalline semiconductor like As$_{20}$Se$_{30}$Ge$_{40}$Te$_{10}$ there is equal or even more compositional disorder but four nearest neighbours forming the familiar tetrahedral covalent bonding surround every Ge atom.

1.16 Electronic Models Of Chalcogenide Glasses:

The carriers in amorphous systems are strongly affected by the randomness of atomic arrangement due to the absence of long-range order. Mott [9] has argued that the spatial fluctuation in the potential, caused by the configurational disorder in amorphous materials may lead to the formation of
localized states, the valence and conduction bands do not have sharp cut off but have a tail above and below the normal band. The extent of these tailing is expected to be enhanced in alloys which contain compositional disorder in addition to positional disorder.

The conduction in localized states take place, by hopping process, with the help of thermal energy. At absolute zero of temperature, no conduction is expected in localized states. The mobility of charge carriers therefore changes suddenly from finite value to zero in the band tails.

Cohen, Fritzsche and Ovshinsky first suggested that in the case of disordered covalent alloys, such as chalcogenide glasses, the valence and conduction band tails overlap each other close to the center of the forbidden gap. The mobility of the carriers has finite value in high density states but it decreases abruptly in tail states (see Fig. 1.5). These boundaries are called mobility edges. The critical energies at mobility edges define a mobility gap.

Davis and Mott [26] proposed that there is a narrow band of compensated localized states, which pin the Fermi level between the two tails (See fig. 1.5). This model suggests that hopping conduction can take place in the localized states near the Fermi level.

Mott and his collaborators [27] further elaborated the model of gap states in chalcogenide glasses. They considered the states near Fermi level due to defects, e.g. dangling bonds. Two electrons are shared in a chemical bond between
Figure 1.5 Various models for amorphous semiconductors.
atoms. In some structural configuration, the atoms are not able to share the electrons and the bond is broken. This is called a dangling bond. A dangling bond is neutral (D$^0$) when occupied by a single electron. In some cases, dangling bond can attract an electron, and become negatively charged (D$^-$), or attract a hole and become positively charged (D$^+$). They based their model on the assumption that paired electron states are preferred in chalcogenide glasses.

In general it is accepted that the localized states in amorphous semiconductors do not correspond to a single energy but have an energy distribution. Various methods, e.g., field effect, space charge limited conduction, deep level transient spectroscopy, barrier capacitance measurement and thermally stimulated currents have been employed to study the localized states in amorphous semiconductors.

The most accepted model for the density of localized states assumes a continuous distribution of localized states having its minimum value near Fermi level. The density of localized states varies with energy on both sides of the Fermi level towards conduction and valence bands.

1.17 Thin Films and their properties:

An independent and important branch of Physical science that has been developed continuously is the Physics of thin films. The name of thin film is not new in the field of science and technology however Bunsen and Grower obtained the thin film in 1852 by explosion of a current carrying metal wire, but it
came to know 1864, when the first solid thin films was obtained by electrolysis. Thin films are used in so many devices such as solar cells, detectors, magnetic memory devices, bolometer, optoelectronics, interference filters, xeroradiography, reflection and anti reflection coating. The progress has also brought much confidence in the use of thin films for basic and applied research. Thin films studies have directly or indirectly advanced many new areas of research in solid state Physics and Chemistry, which are based on the phenomena uniquely characteristic of the thickness; geometry and structure of the films. Thin films have been extensively studied for over a century because of their potential, technical value and scientific curiosity. The study of thin surface films involves several fields of fundamental and practical importance. The film prepared by the use of semiconductors conducting materials is of the most importance in science and technology.

Films of semiconductors conducting materials are of great importance due to their wide use in various solid-state devices also. II- VI group compounds are widely used in solid-state devices such as infra- red detector, photovoltaic cells, nuclear radiation detectors and window for IR laser etc. These are the important semiconductors for opto-electronic devices. This group is much more important for photo- conductive and photo-electric devices [28].

The thin films of semiconductors conducting materials have covered a wide area of the field of technology and research. Now a days these films are the
integral part of large number of devices. In modern technology one can control the physical properties of these films within the limits required for the use by the appropriate range of parameters like the deposition technique rate, substrate temperature and impurity etc. The applications of thin films depend upon the band gap and their nature, position of electron-hole traps in the energy gap, mobility of charge carriers and electron work functions etc.

1.18 Absorption Edge In Chalcogenide Glasses:

Many crystalline semiconductor are opaque similar to the metals in visible portion of the light. However, they are transparent in infrared region. The light photon is observed only when the energy of the light exceeds the energy of the band gap. The transmission through the semiconductor reduces to zero sharply at a particular energy. This is known as optical gap of the semiconductor. At higher energies than the band gap, photon is able to excite an electron occupying a quantum state at the top of the valence band to the quantum state and at the bottom of the conduction band. The crystal thus appears opaque at these energies.

When the quantum states in the gap exist (donor or acceptor levels), transmission may show dips at lower energies also. If thermal energy is kept low (at low temperatures) transmission measurements may be able to determine the energies of donor or acceptor states.
1.19 Utility of Chalcogenide Glasses:

The fact that amorphous semiconductors can be prepared in thin film form which requires simple technology than growing single crystals has made these materials more interesting from device point of view.

Chalcogenide glasses and hydrogenated amorphous silicon have been used for various solid state devices. Given below are some of the uses of these materials.

Chalcogenide glasses are transparent in infrared region and are, therefore, used in infrared lenses. They are not influenced by micro-impurities and moisture and are, therefore, used as moisture proof coatings on various solid state devices.

The photo structural changes are also observed in these glasses. They can, therefore, be used in optical mass memories. These glasses are also found suitable for image converters and intensifiers, ultrasonic delay lines and phase contrast holograms.

Memory switching has found application in computer memories. S.R.Ovshinsky at Energy Conversion Devices Inc, USA, has developed a 1024 bit computer memory using chalcogenide glasses. These are commercially produced and are successfully used in computers.

Since threshold voltage depends upon temperature, the use of chalcogenide glasses in thermalswitch is also suggested. Due to high current
capacity, such switches can be used in automobile engines and large power machines where temperature control is needed.

Chalcogenide thin films show photoconduction in which the volume of the substance changes and density becomes large in presence of Light. This property of chalcogenide glasses is being used in lithography.

Efforts are being made to dope these glasses and then they can be used for others solid state devices where n or p type semiconductors are required.

After the discovery of hydrogenated amorphous silicon which has much smaller density of localized states, Carlson and Wronski [29] first demonstrated that a – Si: H can be used for cheap solar energy conversion. They used a–Si: H Schottky barriers to produce solar cells and obtained an efficiency of about 5.5%. Though the efficiency of a – Si: H cells were smaller than that obtained using crystalline silicon, continuous efforts were made to improve the efficiency. Recently, the efficiency of amorphous silicon solar cells has been increased to 12%.

Amorphous silicon solar cells have been produced commercially [30] and are being used in pocket calculators, watches, radios, clocks etc. The process of fabrication of these cells is much simpler and cheaper as compared to crystalline solar cells. Industrialization is possible for these cells and therefore they have great potential for cheap solar energy conversion.
On the other hand, the sensitivity characteristics of a-Si:H solar cell exactly match with the spectral distribution of the fluorescent light. These cells are, therefore, as efficient in fluorescent light as in sunlight. This property of a-Si:H solar cells makes them suitable for consumer products, e.g. calculators, watches, radios and clocks.

To improve the quality of Chalcogenide glasses material various preparations conditions are changing continuously. Efficient doping in these films are also being tried so that one can make p-n junction and other solid state devices equally good as are made using crystalline silicon. Transport properties, role of hydrogen, light induced effects and amorphous silicon super lattices are the main topics of recent research on these materials.

On chalcogenide glasses also, attempts are being made to dope these glasses and to make n or p-type semiconductors so that they could be used in devices similar to their crystalline counterparts. Various new alloy systems are being explored to find out suitable material, which can be good photoconductor and have potential use in device applications.

Research on the theoretical side is also progressing but not much success has yet been made, as mathematical simplicity does not exist in these materials. Attempts are being made to extend the theories and models, which are already available for crystalline semiconductors. A lot of theoretical work is needed to explain many effects of amorphous semiconductors. Theoretical work is
being done on the same amorphous semiconductors till date by many works. B.T. Kolomiets and his associates in USSR first started working on glasses containing one or more chalcogen elements (S, Se and Te) in large proportions, instead of conventional six group elements, ‘O’ which was used to prepare glasses. They found that these glasses (known as chalcogenide glasses) behave similar to intrinsic crystalline semiconductors. These workers did not consider these semiconductors very interesting, as they could not make n - or p- type semiconductors by doping them with Vth or IIIrd group elements of the periodic table.

In 1968, S. R. Ovshinsky first observed reversible switching in chalcogenide glasses and reported two types of switching, namely threshold and memory. Since then, chalcogenide glasses are being studied in detail by physicists as well as by engineers. Over a span of about 15 years, various solid state devices using these glasses have been developed which include image converters and intensifiers, switching and memory devices continuous dynode electron multipliers, optical mass memories, phase contrast holograms, high energy particle detectors, infrared lenses, ultrasonic delay lines and microfiche transparencies etc.

Other crystalline semiconductors e.g. Si and Ge were also made in the form of non-crystalline films by vacuum evaporation, sputtering, electrolytic deposition and gas discharge. Hydrogenated amorphous silicon is found most
suitable for making p - n junctions, Schottky barriers and other solid state devices.
This material is successfully being used for the cheap solar energy conversion.

Thermodynamic equilibrium does not exist in amorphous state.
However, the thermal energy at room temperature is not sufficient to overcome the
energy barriers to convert an amorphous substance into a crystalline one. When
amorphous substance is heated to high temperatures, it tends towards its
crystalline state with a considerable release of energy. An exothermic peak is,
therefore, observed in differential thermal analysis at the temperatures where
crystallization takes place.

Chalcogenide glasses are being successfully used in computer
memory. These devices are being made at Energy Conversion Devices, Inc, Troy,
Michigan, USA. Using amorphous silicon solar cells, for the last few years, large
scale power generation using mass produced solar cells is also being tried in
various countries. Apart from the application in solar cells, a-Si :H is also being
used in other solid state devices similar to its crystalline counterpart.

1.20 Optical Properties Of Chalcogenide Glasses:

Reflectance and transmittance of light are periodic functions of the
path difference between waves reflected from the air film and film substrate
interfaces respectively. This path difference is related to the angle of incidence and
the wavelength of incident light as well as the film thickness. Hence instead of
monitoring reflectance and transmittance as function of wavelength or angle of
incidence, the variation with film thickness is reported by various workers [31]. In these cases the film thickness change slowly but the optical parameters change rapidly.

Different methods have been developed for the complete analysis of thin films by measurement of reflectance and transmittance measured as a function of wavelength or angle of incidence [32, 33]. For weak absorbing films, several methods are available for the calculation of optical parameters from the envelopes of reflectance and transmittance. However, experimentally it is more convenient and simpler to measure either the reflectance or the transmittance. For this type of films, methods have been developed for complete optical analysis using reflectance measurements alone. The optical constants can be calculated by using the data of reflectance and transmittance on different frequencies [34, 35].

1.21 Optical Absorption and Optical Band Gap:

The optical absorption and optical band gap depend on the short-range order in the amorphous structure and defects associated with it. The variation of the optical band gap and properties of thin films of the present systems deserve a comprehensive investigation.

The mechanism of disorder and defect interaction in amorphous chalcogenide is expected to be understood from the studies of the variation of the optical band gap and the short-range order as a function of thickness for the films of different compositions [36]. The decrease in the disorder and defect states in the
structural bonding is known to increase the optical band gap. Thus, a study concerning the variation of optical band gap as a function of composition for Ge–Se–In and Ge–Se–Ag System thin films may provide deeper insight into the mechanism of disorder and defects formation in amorphous chalcogenides.

1.22 Absorption Process:

These properties span a wide range of phenomena and aid us greatly in understanding the basic physical properties of semiconductors. These properties are also used in the development of optical devices in research and industry.

The measurement of absorption spectra is the direct method for probing the band and structure of semiconductors. In the absorption process a photon of known energy excites an electron from a lower to higher energy state. In a different manner, one can say that absorption is also a result for interaction between atoms and electromagnetic radiation. The specific microscopic interactions between a light wave and a real semiconductor, are important in various part of the spectrum as:

(a) Electron transition from the upper part of the valence band to the lower part of conduction band are responsible for the shape of absorption spectrum near fundamental absorption edge.

(b) Electron transition from deep states in valence band or states high up in the conduction band, govern the optical properties in the short wavelength (ultra violet part of the spectrum).
(c) The interaction of light with lattice vibration governs the absorption in the far infrared region.

In semiconductors a number of distinct optical absorption processes also take place independently. These processes are given as:

**1.23 Fundamental Absorption Process:**

The most important process involves the transition of electrons from the valence to the conduction band (Fig. 1.6). Because of its importance, the process is referred to as fundamental absorption.

In fundamental absorption, an electron absorbs a photon (from the incident beam), and jumps from the valence into the conduction band. The photon energy must be equal to the energy gap or larger. The frequency must therefore be

\[ \nu \geq \frac{E_g}{h} \]  

(1.4)

The frequency \( \nu_0 = \frac{E_g}{h} \) is referred to as the absorption edge. In transition process (photon absorption), the total energy and momentum of the electron – photon system must be conserved. Therefore,

\[ E_f = E_i + h\nu \]  

(1.5)

where \( E_i \) and \( E_f \) are the initial and final energies of the electron in the valence and conduction bands, respectively and \( k_i \) and \( k_f \) are the corresponding electron momenta. The vector \( \vec{q} \) is the wave vector for the absorption photon. However the wave vector of a photon in the optical region is negligibly small. The momentum condition therefore reduces to
That is the momentum of the electron alone is conserved. This selection rule means that only vertical transition in $k$-space is allowed between the valence and conduction band.

Calculating the absorption coefficient for fundamental absorption requires quantum manipulations. Essentially, these consist of treating the incident radiation as perturbation, which couples the electron state in the valence band to its counterpart in the conduction band and using the technique of quantum perturbation theory. One then finds that the absorption coefficient has the form

$$\alpha = A (h\nu - E_g)$$

(1.7)

Where $A$ is a constant involving the properties of the bands and $E_g$ is the energy gap. The absorption coefficient increases parabolically with the frequency above the fundamental edge. Thus $E_g$ is directly related to the frequency edge $E_g = \frac{h \nu}{2}$. This is now the standard procedure of determining the band gap. The optical method also reveals many more details about the band structure than the conductivity method.

The absorption coefficient associated with fundamental absorption is large, about $10^4 \text{ cm}^{-1}$. Thus absorption is readily observable even in thin samples. Since the energy gaps in semiconductors are small (1 eV or less), the fundamental
edge usually occurs in the infrared region. Because of this, study of the infrared region of the spectrum has been greatly expanded by semiconductor research.

The absorption process occurs in the so-called direct-gap semiconductors. Here the bottom of the conduction band lies at $k = 0$ and hence directly above the top of the valence band. Electrons near the top of the valence band are able to make transitions to state near the bottom of the conduction band following the selection rule. Example of such substance is GaAs, InSb and many other III-V compounds.

There are also indirect-gap semiconductors, in which the bottom of the conduction band does not lie at the origin (Fig 1.7). In this case, the electron cannot make a direct transition from the top of the valence band to the bottom of the conduction band because this would violate the momentum selection rule.

Such a transition may still take place but as a two step process. The electron absorbs both a photon and a phonon simultaneously. The photon supplies the needed energy, while the phonon supplies require momentum.

Calculation of the indirect-gap absorption coefficient, which is more involved than that of direct absorption, shows that the formula is given by [37]

$$\alpha_i = A'(T)(\hbar \nu - E_g)$$

(1.8)

Where $A'(T)$ is a constant containing parameters pertaining to the bands and the temperature. Here $\alpha_i$ increases as the second power of $(\hbar \nu - E_g)$, much faster than the half power of this energy differences, as in direct transition.
Figure 1.6 The fundamental absorption process in semiconductors

Figure 1.7 An indirect gap semiconductor.
So, one may use the optical method to discriminate between direct and indirect gap semiconductors as improvement over the conductivity method.

1.24 **Exciton Absorption:**

In the discussion of fundamental absorption, it is assumed that the excited electron becomes a free particle in the conduction band and similarly, the hole left in the valance band is also free. The electron and hole attract each other, however, these may possibly form a bound state, in which the two particles revolve around each other. Such a state is referred as an exciton. The binding energy of the exciton is small, about 0.01 eV and hence the excitation level falls very slightly below the edge of the conduction band as indicated in fig. 1.8.

\[ h\nu = E_g - E_{ex} \]  

(1.9)

Where \( E_{ex} \) is the excitation binding energy. The excitation spectrum therefore consists of a sharp line, falling slightly below the fundamental edge. This line is often broadened by interaction of the excision with impurities or other similar effects and well merge with the fundamental absorption band, although often the peak of the exciton line remain clearly discernible. This illustrate a fact which is often observe that the absorption of an exciton introduces complications into the fundamental absorption spectrum, particularly near the edge and the determination of the energy gap in semiconductors more difficult. However, exciton absorption is important in the discussion of optical properties of insulators in the ultraviolet region of the spectrum.
1.25 Free Carrier Absorption:

Free carriers both (electrons and holes) absorb radiation without becoming excited in to the other band. In absorbing a photon, the electron (or hole) in this case makes a transition to another states in the same band as shown in figure 1.9. Such process is usually referred to as an interband transition. For concreteness, take the substance to be n-type, so that only electrons are present. The real and imaginary parts of the dielectric constant are given by

\[ \varepsilon'_r = \varepsilon_{tr} \cdot \frac{\sigma \varepsilon_0}{\varepsilon_0} (1 + \omega^2 \tau^2) = n_0^2 - k^2 \] \hspace{1cm} (1.10)

\[ \varepsilon''_r = \frac{\sigma \varepsilon_0}{\varepsilon_0} \omega (1 + \omega^2 \tau^2) = n_0 k \] \hspace{1cm} (1.11)

At low frequency and small conductivity (low concentration) the lattice contribution dominates the dielectric polarization. Thus the substance acts as a normal dielectric. There is however, a slight absorption associated with \( \varepsilon'_r \) which represents the absorption of radiation by free carriers.

In the region of low frequency and high conductivity the free carrier term in equation (1.9) dominates. Thus \( \varepsilon'_r < 0 \), and the substance exhibits total reflection such as a metal does. In the high frequency (short wave length) region \( \omega \tau >> 1 \) (But small conductivity) the materials acts like a normal dielectric with \( n_0 \) \( \omega \tau \), and the absorption coefficient is

\[ \alpha = \frac{\sigma_0}{\varepsilon_0} \cdot c n_0 \omega^2 \tau^2 \] \hspace{1cm} (1.12)
Figure 1.8 Exciton level and associated absorption.

Figure 1.9 Free carrier absorption.
The free carrier absorption take even when $h\nu < E_g$ and frequently this absorption dominates the spectrum below the fundamental edge. For $h\nu > E_g$ both types of absorption, fundamental and free, carrier occurs simultaneously.

1.26 Absorption Process Involving Impurities:

Absorption process involving impurities often take place in semiconductors. The type and degree of absorption depend on the type of impurity present in the concentration. Figure 1.10 depicts the main classes of such processes. Figure 1.10 (a) shows the case in which a neutral donor absorbs a photon and the electron makes a transition to a higher level in the impurity itself or in the conduction band. The transition to higher impurity levels appears as sharp lines in the absorption spectrum. Figure 1.10 (b) shows the transition from the valance band to a neutral acceptor, which is analogous to the donor-conduction band transition. Figure 1.10 (c) indicates the absorption spectrum associated with the valance band and acceptor transition in Si.

The spectrum may also serve as a diagnostic technique for determining the type of impurity present. Figure 1.10 (d) represents a process in which an electron is excited from the valance band to an ionized donor or forms an ionized acceptor in the conduction band. Such processes lead to absorption which is close to the fundamental absorption and are seldom resolved from it. Figure 1.10 (e) illustrates an absorption process involving transition from an ionized acceptor to an ionized donor. The energy of the photon in this case is
Figure 1.10 Various absorption processes involving impurities
This leads to a discrete structure in the absorption curve, but this is often difficult to resolve because of its proximity to the fundamental edge.

Impurities may also affect the absorption spectrum in other, different ways. For instance an exciton is often found to be trapped by an impurity. This may happen as follows: The impurity first traps an electron and once this happens the impurity now charged and attracts a hole through the coulomb force. Thus both an electron and a hole are trapped by the impurity. The spectrum of this exciton is different from that of a free exciton because of the interaction with the impurity.

1.27 Optical Constants of Thin Films:

The optical behaviour of a material is generally utilized to determine its optical constants, refractive index ($\nu$) and coefficient of extinction ($k$). Films are ideal specimen for reflectance and transmittance type of measurements. Separate determinations of $\nu$ and $k$ can be made by measuring reflectance and transmittance of the same specimen. To find these optical constants from reflectance and transmittance data obtained from spectrophotometric measurements, the under written procedure is used. The theory for reflectance of light from a thin film is well known and is expressed in terms of Fresnel’s coefficients as given by [38]

$$r_p = \frac{n_0 \cos \phi_1 - n_1 \cos \phi_0}{n_0 \cos \phi_1 + n_1 \cos \phi_0}$$ (1.14)
The thesis of Mala Shukla

\[ r_{p} = \frac{n_{0} \cos \phi_{1} - n_{1} \cos \phi_{0}}{(n_{1} \cos \phi_{1} + n_{0} \cos \phi_{0})} \]  \hspace{1cm} (1.15)

\[ t_{p} = \frac{2n_{1} \cos \phi_{1}}{(n_{0} \cos \phi_{1} + n_{1} \cos \phi_{0})} \]  \hspace{1cm} (1.16)

\[ t_{s} = \frac{2n_{1} \cos \phi_{1}}{(n_{1} \cos \phi_{1} + n_{0} \cos \phi_{0})} \]  \hspace{1cm} (1.17)

where \( n_{0} \) and \( n_{1} \) are the refractive indices of two isotropic media \( \phi_{1} \) is the angle of incidence of light at the interface \( n_{0}/n_{1} \) is the angle of refraction \( t_{p} \) and \( t_{s} \) are the ratio of the amplitude of reflected to incident light or Fresnel’s reflection coefficients for plane polarized components in which the electric vector lies parallel (p) and perpendicular (s) to the plane of incidence and \( t_{s} \) is the amplitude of transmitted to incident light. Using Snell’s laws, we have

\[ \frac{n_{0} \sin \phi_{0}}{n_{1} \sin \phi_{1}} \]  \hspace{1cm} (1.18)

Rewriting equation (1.13) and (1.14), the reflectivity \((R)\) of an interface can be given as

\[ R_{p} = R_{s} = t_{p}^{2} = t_{s}^{2} \]  \hspace{1cm} (1.19)

Since the reflected and incident beams are in the same media.

Similarly the transmittance \((T)\) can be given as

\[ T_{p} = \frac{(n_{0}/n_{1})r_{p}}{r_{p}^{2}} \]  \hspace{1cm} (1.20)

\[ T_{s} = \frac{(n_{0}/n_{1})r_{s}}{r_{s}^{2}} \]  \hspace{1cm} (1.21)

For normal incidence at \( n_{1}/n_{0} \) interface

\[ R = R_{p} = R_{s} = \left[ (n_{1} - n_{0})/(n_{1} + n_{0}) \right]^{2} \]  \hspace{1cm} (1.22)
For air as one medium $n_0 = 1$ and considering film as second medium which is highly absorbing in nature, the above relations can be rewritten as

\[
R = \frac{((n_1 - 1)^2 + k_i^2)}{((n_1 + 1)^2 + k_i^2)}
\]  

(1.24)

Where $k_i$ is the extinction coefficient of the film.

This relation is valid in the wavelength region where interface effects are negligible. Further, these relations can be applied to the films deposited on non-absorbing substrate with refractive index smaller than that of the film. The transmittance of the film (in the interference free region) is given by

\[
T = \frac{[1 - R_1)(1 - R_2)(1 - R_3).e^{-\alpha t}]}{(1 - R_2R_3)[1 - [R_1R_2 + R_1R_3(1 - R_2)].e^{-2\alpha t}]} 
\]  

(1.25)

where $R_1$, $R_2$ and $R_3$ are the reflectances at the air film, film substrate and substrate air interfaces respectively. Neglecting $R_3$ and assuming $R_1$ and $R_2$ to be equal to the measured reflectance ($R$) relation (eqn. 1.25) reduces to

\[
T = \frac{[1 - R)^2.e^{-\alpha t}]}{[(1 - R)^2.e^{-2\alpha t}]} 
\]  

(1.26)

where $\alpha$ is the absorption coefficient and the relation between absorption coefficient $\alpha$ and extinction coefficient $k$ is given by

\[
\alpha = \frac{4\pi k}{\lambda}
\]  

(1.27)

Thus using relations (1.14 to 1.27) one can find out the values of absorption coefficient ($\alpha$), refractive index ($\theta$) and extinction coefficient ($k$).
The absorption coefficient ($\alpha$) can also be calculated directly from the absorbance versus wave number curves using the relation [39].

\[
OD = \frac{\log \frac{I_B}{I_i}}{I_1} = \alpha t
\]  \hspace{1cm} (1.28)

\[
\alpha = \frac{OD}{t}
\]  \hspace{1cm} (1.29)

O.D. is the optical density measured at a given layer thickness $t$ (cms). $I_B, I_i$ are the intensities by light radiation and transmittance respectively.

1.28 Application of Thin Film of Amorphous Semiconductor:

In recent year, optical memory effects in amorphous semiconductors have been investigated and utilized for various applications. These have distinct advantages, viz. large packing density, possible achievability, mass replication, fast data rate, high signal to noise ratio and high immunity to defects [40- 43]. Glassy chalcogenide semiconductors have great varieties of band gap. The use of these thin films for reversible optical recording by the amorphous crystalline phase change has recently been reported by a number of workers [44-47]. The chalcogenie used for the recording media must be easy to amorphize and crystalline and there should be a high optical contrast between the amorphous and crystalline states. Further more, the writing and erasing must be fast and the materials should be stable on an adequate number of write and erase cycles.

All optical storage media share the basic principle of storing information by altering some optical properties of the media by selective exposure
to light using laser of suitable wavelength [48]. This result is a contrast between
the background and the written (laser annealed) portion of the film. The difference
in reflectance is used to read the data while suitable intensity of the same laser
may used for erasing.

1.28 The Absorption Edge:

The absorption edges of amorphous germanium [49] and amorphous
gallium arsenide [50] are shown in Fig. 1.11. The materials were prepared by
sputtering onto cool substrata in an atmosphere of argon to which different
quantities of hydrogen were added. The incorporation of the hydrogen into the
samples has been studied in great detail, but for the purpose of this discussion, it is
sufficient to recognize that a large fraction forms between bonds and with
individual dangling bonds on the void surfaces. Thus, the optical properties of
fully bonded but hydrogenated material, which near the gap, will resemble those
of fully coordinated material. The absorption edge position and, to a lesser extent,
shape are dominated by the effects of voids and the optical properties of fully
coordinated material cannot be straightforwardly deduced.

Another complication exists in these materials is exhibited in
Fig. 1.12. The hydrogenated germanium specimens of Fig. 1.11 were annealed for
one hour at 250°C and their absorption edges measured. Although the changes
in absorption were largest in samples with least hydrogen. Changes were observed
even in those, which had complete hydrogen coverage of the void surfaces. It must
Figure 1.11(a) Absorption coefficient versus photon for Ge$_{1-x}$H$_x$ films: •••• 0, xx xx 0.01, ????, 0.028, ? ? ? ? 0.03, ????, 0.051, oooo 0.08. Estimates o the error in a are shown for two of the films (b) Absorption coefficient versus photon energy for hydrogenated GaAs film.
Figure 1.12 Absorption coefficient versus photon energy for Ge$_{1-x}$ H$_x$ films after a 250°C anneal for one hour: ..., xxx 001, ?? 0.028, ?? 0.03, ??? 0.051, and ooo 0.08. Data for films produced at $T_s$ = 250°C are also shown: --- 0.01 and +++ 0.042. Estimates of the error in x are shown for one of the films.
be assumed then that annealing produces absorption edge shifts both by dangling bond removal and by network reorganization, and even in fully coordinated material, the absorption edge might not have a unique form.

A more quantitative examination of these data for amorphous germanium and gallium arsenide indicates that for any particular thermal history the absorption edge, and $\varepsilon_1 (0)$ also exhibit asymptotic behavior with hydrogen coverage. In this case, the absorption below $10^4 \text{ cm}^{-1}$, depends exponentially on photon energy and is represented by Maschke et al. [51], whereas above $10^4 \text{ cm}^{-1}$, it is represented by the power law of Hindley [52]. However, the exponential edge is steeper and the power law edge begins at higher energy than in unhydrogenated material. For example in annealed germanium specimens, $\beta$ changes from 8.3 to 167eV, and $E_0$ increases from 0.8 to 1.1 eV with hydrogenation.

1.29 Exponential Absorption Region:

The exponential absorption in unhydrogenated material is consistent with a model in which each band edge has an exponential tail. If it is further assumed that the valence and conduction bands are symmetric and the Fermi level is pinned at the center of the gap, it is possible to make a rough estimate of the density of state in the gap from the absorption measurements directly. The unreasonable result of the material is a density of state at the Fermi level of $3\times10^{19}$ cm$^{-3}$ [53]. However the uniqueness of this estimate will be taken up again later.
An identical analysis of annealed or hydrogenated material would obviously demonstrate a decrease in the density of gap states and it seems appropriate, to associate the exponential absorption in partially coordinated material with transitions involving the electronic states of the void surfaces. A quantitative relation of this kind was first suggested for evaporated amorphous silicon by Brodsky and Kaplan [54]. They argued that at an energy (E) the density of states Q(E) could be approximately written as

$$Q(E) \approx Q_0(E) + Q_s(E)n_s.$$  \hspace{1cm} (1.30)

where $Q_0(E)$ is the bulk density of states, $Q_s(E)$ is proportional to the surface density of states per dangling bond, and $n_s$ the electron spin density.

The equation 1.30 is assumed to be a direct measure of the number density of dangling bonds. Then using [55] the absorption coefficient becomes

$$\alpha(\omega) \approx a_0(\omega) + a_1(\omega)n_s + a_2(\omega)n_s^2.$$  \hspace{1cm} (1.31)

where $a_0$, $a_1$, and $a_2$ are constant coefficients at fixed photon energy.

Thus the observed dependence of the absorption edge on the spin concentration not only permits the derivation of the absorption edge in fully coordinated material but it emphasizes the extent to which void-related states create the exponential absorption. In the case of unhydrogenated sputtered amorphous germanium and evaporated amorphous silicon, the major role of voids is incontrovertible. Nevertheless, the extent to which potential fluctuations associated with these voids generate the exponential edge by establishing an exponentially varying matrix
element is not known, and consequently the estimate of the number of gap states based on an exponential distribution of them must be treated with some caution.

From the dependence on hydrogenation, it also appears that the major contribution to the exponential absorption in unhydrogenated amorphous gallium arsenide is from transitions involving surface state on voids rather than from those involving like-bonds. One possibility is shown in Fig. 1.13. Because of surface relaxation, the onset of optical absorption arises from transitions between the valence band edge and empty p states on three coordinated gallium atoms [56]. This scheme thus rationalizes not only the effects of hydrogenation but also the puzzling result; found in early investigations of amorphous III-IV compounds, that the location of the exponential edge depended predominantly on the group III atom and to a much lesser extent on the group V atom.

The possibility that potential fluctuations associated with hydrogen-covered void surfaces give rise to the steeper exponential absorption in fully hydrogenated amorphous germanium. Street [57] points out another contribution to the absorption, at least in glow discharge-deposited amorphous silicon, that arises from transitions between the states of the fully coordinated material. In Fig 1.14, the luminescence line at 1.3eV is shown in relation to its excitation spectrum. The relative position of them indicates a Stokes shift of about 0.5 eV and therefore a distortion energy \( W_p \) of about 0.25eV. A phonon-broadened edge, given by [58], must therefore occur. By applying detailed balance, the absorption strength
Figure 1.13 Schematic representation of atomic relaxation on a void surface of a III-V amorphous semiconductor. The solid arrows show the direction of atom movement during the relaxation and broken arrows show the direction of electron transfer. Similar models can be applied equally well to void surfaces of group IV amorphous semiconductor. (b) The electronic states associated with the relaxed surface of amorphous GaAs.
Figure 1.14 Photoluminescence spectrum (PL), excitation spectrum, and room-temperature absorption in glow-discharge-deposited amorphous silicon.
associated with the luminescence band may be calculated from its radiative lifetime. Clearly, a phonon-broadened component of absorption makes significant contributions to values $10^2 - 10^3 \text{ cm}^{-1}$, and its magnitude and energy dependence is not greatly different from the measured absorption.

1.30 Power Law Absorption Region:

If the densities of states of the valence and conduction band edges are assumed to have the same parabolic dependence, $g(E)$, they may be found by applying [59] directly to the absorption spectrum. It is particularly interesting to note, however, that in both cases $g(E)$ is very close to the free electron value $g_f$, given by

$$g_f(E) = 6.7 \times 10^{21} (\Delta E)^{1/2}$$

(1.32)

where $\Delta E$ is the departure from the band edge. Qualitatively similar results are also obtained for the effects of hydrogenation although a larger variation of $E_0$ can be induced. In fact, at full coverage in annealed specimens, $E_0$ reaches about 1.1 eV.

In the early literature, the relation of $E_0$ to the band gap of the crystal was much considered, but the effects of voids often produced misleading or evidently conflicting experimental results. From the above discussion, however, it would seem that $E_0$ is larger, though not directly related to the crystalline gap. The same conclusion is also reached in amorphous silicon for which $E_0$ in the void-free materials is estimated, either from [60, 61] or from hydrogenated material [62], to
be about 1.8 eV. The band gap in theoretical calculations is extremely sensitive to the topology of the network, such a result is not surprising. In fact, it may represent the effect of five-membered atomic rings in the amorphous phase, masked by the opposing effect of quantitative disorder.

The absorption spectra, with a rapid rise in absorption at shorter wavelength can be used to determine the energy band gap of the semiconductor. Every solid has its own characteristics energy band structure. The conduction and valence band are the regular features of all the solids. Only difference is upto which they are occupied and vertical separation between them i.e. energy band gap. Thus energy band gap may be defined as the gap or region between the valence and conduction band in which there is no level of energy. The band gap may be classified as direct and indirect band gap depending upon the electron transition.

1.31 Direct and indirect band gap:

As the photon of incident light is absorbed by the material, an electron is excited from lower to upper energy level or state. This transition of electron can be direct (without phonon participator) or indirect (in which the interaction with a phonon takes place). In a direct transition an electron in the conduction band can fall (Fig. 1.15) to an empty state in the valence band giving off the energy difference \( E_g \) as photon of light. On the other hand, if an electron in the conduction band can’t fall directly to the valence band but must under go a
Figure 1.15 (a) Direct and (b) Indirect band gap.
momentum change as well as changing its energy the transition is called in direct. The differences between direct and indirect band structure is very important for deciding that which semiconductor can be used in device requiring light output.

1.32 Determination of the energy band gap (Eg):

The absorption spectrum of material is an important technique, which is used for measuring the energy band gap (Eg) of semiconductor. An important feature of this method is that it is applicable for any range i.e. narrow or wide bands gap materials.

Let a photon beam of intensity I₀ (photons/cm² sec) is incident at the sample of thickness t and the intensity of light transmitted is Iₜ then.

\[ I_t = I_0 e^{-\alpha t} \]  \hspace{1cm} (1.33)

Where \( \alpha \) is absorption coefficient and has unit cm⁻¹. The coefficient varies with photon wavelength and also with the materials. Discrimination between direct and indirect transition is possible on the basis of the dependence of absorption coefficient on photon energy. The various type of transition give rise to different frequency dependent absorption coefficient near the fundamental absorption edge for direct transition, we have

\[ \alpha \nu = A (\nu - E_g)^n \]  \hspace{1cm} (1.34)

where

\[ \nu = \text{Photon energy} \]
\[ E_g = \text{Band gap} \]
\[ \alpha = \text{Absorption Coefficient} \]
\[ n = 1/2, 2, 3/2, 3 \]
\[ A = \text{Constant} \]
\[ n = 1/2, \text{Allowed direct transition} \]
\[ n = 3/2, \text{Forbidden direct transition} \]
\[ n = 2, \text{Allowed indirect transition} \]
\[ n = 3, \text{Forbidden indirect transition} \]

The indirect transitions give rise to relation
\[ \alpha hv = A(hv - E_g')^n \]  \hspace{1cm} (1.35)

where \( E_g' = E_g \pm h v_{pn} \) and \( v_{pn} \) is frequency of phonon.

\( n = 2 \) provides the allowed transition

In case of direct band gap the allowed transition are given by using the equation:
\[ \alpha hv = A(hv - E_g)^{1/2} \]  \hspace{1cm} (1.36)

A plot of \((\alpha hv)^2\) versus photon energy \((h?g)\) when extrapolated to zero absorption provide the value of energy band gap.

While in case of indirect band gap the allowed transitions are given by using equation:
\[ \alpha hv = A(hv - E_g)^2 \]  \hspace{1cm} (1.37)

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For a single phonon frequency the plot of $(\alpha \hbar \nu)^{1/2}$ versus photon energy $(\hbar \nu)$, when extrapolating to zero absorption gives

\[ E_g \text{ i.e. } E_g + E_{pn} \text{ and } E_g - E_{pn} \]

where \( E_{pn} = \hbar \nu_{pn} \) (phonon energy)

1.33 Optical transmission:

Let a light beam of intensity \( I_o \) be made incident on a surface and \( I \) be intensity of transmitted beam, then the ratio of transmitted to incident intensity \( \frac{I}{I_o} \) is termed as the transmission coefficient. If \( \alpha \) is the absorption coefficient, \( t \) is the thickness and \( R \) is the reflectivity then the radiation transversing the first interface is \((I - R) I_0\). The radiation reaching the second interface is \((I - R) I_0 \exp(-\alpha t)\) and only a fraction of \((I - R) (1 + R) I_0 \exp(-\alpha t)\) emerges. The internally reflected portion comes out after a considerable attenuation.

Thus the resultant i.e. the overall transmission is given by:

\[ T = \frac{(I - R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \quad (1.38) \]

when the product \( \alpha t \) is large the second term in the denominator can be neglected such that

\[ T = (1 - R)^2 \exp(-\alpha t) \quad (1.39) \]
1.34 Determination of optical constants:

The optical behaviour of a material is generally utilized to determine the optical constants \( \varepsilon \) (refractive index), \( k \) (extinction coefficient), \( \varepsilon \) (dielectric constants) and \( t \) (thickness). The thin films are ideal specimens for reflection, transmission and absorption measurements. Several of these methods actually determine the effective optical thickness from which the material thickness of the film can be derived, provided that the optical constants are known and vice versa.

We use transmission method for determination of \( \varepsilon \) & \( k \).

1.35 Transmission Method for determination of \( \varepsilon \) & \( k \):

Fig. (1.16) represents a thin film with a complex refractive index, \( \eta \) = \( \varepsilon \) - \( k \) bounded by two transparent media of indices \( \eta_0 \) and \( \eta_1 \).

For normal incidence the transmittance is given by:

\[
T = \frac{16\eta_0 (\eta^2 + k^2)\eta_1 P}{A + BP^2 + 2P[C \cos \left( \frac{4\pi \eta}{\lambda} \right) + D \sin \left( \frac{4\pi \eta}{\lambda} \right)]}
\]  

(1.40)

where

\[
A = [(\eta + \eta_o)^2 + k^2][(\eta + \eta_i)^2 + k^2]
\]

\[
B = [(\eta - \eta_o)^2 + k^2][-(\eta - \eta_i)^2 + k^2]
\]

\[
C = -[(\eta^2 - \eta_o^2 + k^2)(\eta^2 - \eta_i^2 + k^2) + 4k^2\eta_0\eta_1]
\]

\[
D = 2k\eta_i(\eta^2 - \eta_o^2 + k^2) + 2k\eta_o(\eta^2 - \eta_i^2 + k^2)
\]

\[
P = \exp \left( -\frac{4\pi kt}{\lambda} \right)
\]

(1.41)

with conditions
Figure 1.16 Reflection and Transmission Phenomena at normal incidence
Which are satisfied if the absorption is weak enough, we obtain.

\[ \begin{align*}
  A &= (\eta + \eta_o)^2 (\eta + \eta_i)^2 \\
  B &= (\eta - \eta_o)^2 (\eta - \eta_i)^2 \\
  C &= -(\eta^2 - \eta_o^2) (\eta^2 - \eta_i^2) + 4k^2 \eta_o \eta_i \\
  D &= 2k \eta (\eta^2 - \eta_o^2) + 2k \eta (\eta^2 - \eta_i^2)
\end{align*} \]

It is easy to show that \( D < C \). So near an extremum we can neglect \( D \).

\[ \sin \left( \frac{4\pi \eta}{\lambda} \right) \]

Moreover, in the most practical case

\[ n_0 < ? > ?_1, \] leads to

\[ \frac{4 \eta_o \eta_i}{(\eta + \eta_o)(\eta + \eta_i)} < 1 \]

and so \( 4k^2 \eta_o \eta_i \ll (\eta^2 - \eta_o^2)(\eta^2 - \eta_i^2) \)

if \( k^2 \ll (? - ?_0)(? - ?_1) \),

then \( T = \frac{16\eta_o \eta^2 \eta_i^p}{C_1^2 + C_2^2 \eta^2 + 2C_1C_2 \eta \cos \left( \frac{4\pi \eta}{\lambda} \right)} \)

where

\[ \begin{align*}
  C_1 &= (\eta + \eta_o)(\eta_1 + ?) \\
  C_2 &= (\eta - \eta_o)(\eta_1 - ?)
\end{align*} \]

The condition for maxima and minima are:

\[ \lambda_{\text{max}} = \frac{4\pi \eta}{2m}, \text{ where } m = 1, 2, 3 \]
\[ \lambda_{\text{min}} = \frac{4\eta_1}{2m+1}, \text{ where } m = 0, 1, 2, 3 \] (1.47)

The extreme values of transmittance are given by:

\[ T_{\text{max}} = \frac{16\eta_0^2 \eta_1 P}{(C_1 + C_2 P)^2} \] (1.48)
\[ T_{\text{min}} = \frac{16\eta_0^2 \eta_1 P}{(C_1 - C_2 P)^2} \] (1.49)

By combining equation (1.48) and (1.49) Lyashenko and Miloslavskil developed an iterative method allowing the determination of \( n \) and \( P \) and using equation (1.41), (1.48) and (1.47) we can get \( k \) and \( t \).

Consider \( T_{\text{max}} \) an \( T_{\text{min}} \) as the continuous functions of \( \lambda \) through \( \lambda(\lambda) \) and \( P(\lambda) \). These functions are the envelopes of the \( T_{\text{max}}(\lambda) \) an \( T_{\text{min}}(\lambda) \) in the transmission spectra of the film.

From eq. (1.48) and (1.49) we have

\[ P = \frac{c_1}{c_2} \begin{bmatrix} \frac{T_{\text{max}}}{1-T_{\text{max}}} \\
\frac{T_{\text{min}}}{1+T_{\text{max}}} \\
\frac{T_{\text{max}}}{1-T_{\text{min}}} \end{bmatrix} \] (1.50)

Then from eq. (1.48)

\[ \eta = [N + (N^2 - \eta_0^2 \eta_1^2)^{1/2}]^{1/2} \] (1.51)

where \( N = \frac{\eta_0^2 + \eta_1^2}{2} + 2\eta_0\eta_1 \left[ \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} T_{\text{min}}} \right] \) (1.52)
equation (2.48) shows that \( \theta \) is explicitly determined from \( T_{\text{max}} \), \( T_{\text{min}} \), \( \theta_0 \) & \( \theta_1 \), at the same wave length.

Knowing \( \theta \) we can determine \( P \) from equation (1.51). The thickness of the film can be calculated from two extrema using equation (1.41) and (1.47).

\[
t = \frac{M \lambda_1 \lambda_2}{2[\eta(\lambda_1)\lambda_2 - \eta(\lambda_2)\lambda_1]}
\] (1.53)

Where \( M \) is the number of oscillations between two extrema (\( M = 1 \), between two consecutive maxima or minima), \( \lambda_1 \) ? \( \lambda_1 \), \( \lambda_2 \) and \( ? \) \( \lambda_2 \) are the corresponding wavelength and indices of refraction. Knowing \( t \) and \( P \) we are able to calculate the extinction coefficient \( k \) from:

\[
k = \frac{\lambda}{4\pi} \frac{1}{\eta(P)}
\] (1.54)

1.36 Determination of dielectric constants:

Complex dielectric constants is given by

\[
\varepsilon^* = \varepsilon' - i \varepsilon''
\] (1.55)

we know the relation between complex dielectric constant and complex refractive index is given by

\[
\varepsilon^*(\lambda) = \eta^*(\lambda)
\]

or

\[
\varepsilon' = (\eta - ik)^2
\] (1.56)

\[
\varepsilon' - i \varepsilon'' = \eta^2 - k^2 - 2i\eta k
\]

equating real and imaginary parts we get
In this way from equations (1.57) and (1.58) we can determine $\varepsilon'$ (real part of dielectric constant) & $\varepsilon''$ (dielectric loss) after determining $\theta$ & k from transmission spectra.