EFFECT OF TRANSITION METAL DOPING ON DC AND AC CONDUCTIVITY OF ARSENIC SULPHIDE

Chapter 3
3.1 INTRODUCTION

Investigation made by different investigators, provided clear evidence that significant modifications in the properties of chalcogenide glasses can be achieved by adding certain impurities [80-84]. The addition of impurities to chalcogenide semiconductors changes the conductivity in the material. The effect of impurities is attractive because, by controlling the amount of dopant, the material can be modified for various device applications.

In other words, chalcogenide glasses can be optically alloyed with metals such as Silver, and in addition, Ag-alloyed chalcogenide glasses exhibit interesting photoinduced phenomenon [111-114]. Among these the most famous may be the so-called photodoping phenomenon, in which an alloying process of a metal, such as Silver, and a chalcogenide glass is dramatically enhanced with illumination. The phenomenon may be promising for ultrahigh-resolution photolithographic processes and for fabricating optical components [115-117]. The chalcogenides (particularly As-S and Ge-Se) have been found to be promising resist materials for photolithography in sub-micron region [85].

In this chapter, temperature and frequency dependence of photo and thermal doped Arsenic Trisulphide (Ag-As$_2$S$_3$) and bulk doped Fe-As$_2$S$_3$ system is studied.
3.1.1 Effect of Impurities in Amorphous Semiconductors

The role of impurity in amorphous semiconductors is unique and our knowledge is far from being complete. But whatever little we know, is interesting from the basic as well as applied aspects. Silver doping in As$_2$Se$_3$ produces large conductivity changes. The conduction mechanism also changes from bipolaron hopping type to single polaron hopping type [86]. In general, most of the doping studies reveal that transition metal impurities, whose atoms have partially filled valance shells, produce a large influence on the electrical properties of As$_2$Se$_3$ [86].

As$_2$S$_3$ is another important glass which belongs to the same category of materials. Its application in the field of IR fibre optics [72], offset printing [87] etc. have been reported. Application of As$_2$S$_3$ as a photo-resist has also been investigated by different groups of investigators [71, 88]. It is therefore, desirable to study the effect of transition metals doping on electrical properties of As$_2$S$_3$.

The work reported in this chapter is a step in this direction. Transition metal doping is expected to produce prominent effects on the electrical properties of As$_2$S$_3$. An inclusive study of temperature and frequency dependent of ac conductivity can give information about the defect states and conduction mechanism.

3.1.2 Dissolution of Transition Metals into Chalcogenide Glasses

The diffusion/electro migrations of transition metals in amorphous semiconductors are well known [89-74]. The rate of diffusion (electro migration) in a given amorphous semiconductor, of course, depends upon the metal and the operating temperature. For example, Silver and Aluminium diffuse so fast even at room temperature that only some
traces of the element are seen sticking on the surface of the sample after a couple of hours [91].

The diffusion/electro migration of electrode-elements into amorphous semiconductors could lead to two serious problems [74, 75, 77, 89-91]. It could alter the basic characteristics of the materials and/or create a lack of metallic contact on surface of the material. It is well known that transition metals have a tendency of diffusion into amorphous materials. This, evidently, could change their characteristics during the course of measurements. In order to avoid the associated problems due to diffusion, some investigators preferred to use uncovered (naked) samples and reported their measurements without depositing an electrode-element. The absence of a conducting film (electrode-element) would eventually amount to the existence of a lack of metallic contact between the surface of the samples and electrode of the cell.

Some of amorphous semiconductors have large conductivity with high temperature dependence. Light radiation can enhance diffusion of transition metals into amorphous semiconductors (evidently, light radiation induces changes in the conductivity behaviour as well as in the structure of amorphous semiconductors) [92-97].

The most widely studied amorphous materials for photo-diffusion are chalcogenide glasses. Kostyshin et al [98] were the earliest reporters in the photo-diffusion, who showed that chalcogenide glasses films, deposited on metal substrates, produced visible images upon exposure to UV radiation. Since then, the phenomenon has been extensively studied and several technological applications have been reported [98-117]. The original application of this process involved the development of an image technology for holographic as well as image recordings [99-101]. A good image
could be obtained by exposing a transition metal-chalcogenide glass structure (Fig. 3.1) to light of wavelengths, smaller than the optical absorption edge of chalcogenide glass [102]. The quality and resolution of the image were reported to be better than those obtained by conventional emulsion films. Another important application of photodoped chalcogenide glasses as photo-resist is in the area of microelectronics [103, 104] (Fig. 3.2). These were found to provide high contrast and high resolution. One-micron features could be easily obtained while submicron features were generated by electron beam exposure [104]. A dry-development process based on As$_2$S$_3$ was also reported [105].

The extensive studies of the mechanism and application have followed. The mechanism has not been elucidated; the reason may be due to the complication inherent in amorphous materials and to varied observation in different samples. The photodoping phenomenon (photo-diffusion or photo-dissolution) is observed in metal/chalcogenide layer structures, in which light illumination induces a fast diffusion of metallic species [118]. Exposure may be provided from the chalcogenide side or from the metal side, if the materials are half transparent.

These inorganic resist polymer bi-level systems [106] were observed to overcome several difficulties encountered in optical lithography, for example, standing wave related problems. It also allowed features of different sizes to be exposed simultaneously.
**Fig. 3.1**, Fine-particle image transfer [110].

(a) Direct shadowing of fine particle.

(b) Direct Photodoping from a Transition Metal Ag fine particle.

**Fig. 3.2**, Photo Dissolution of a Transition Metal in Chalcogenide Glasses.
3.1.3 Mechanism of Photodoping

Ishikawa [107] proposed that the light de-ionises some charged defects ($D^+ + D^- + \nu \rightarrow 2D^0$) in undoped chalcogenide glasses and meta-stable $D^0$ states trap the electrons donated by metal. The so formed ion (e.g. $Ag^+$) is pulled by $D^-$ states into the chalcogenide glass. This model implied that the actinic light is absorbed in the undoped glass adjacent to the already doped material. However, this model was unable to explain why photodoping ceases when the metal source layer is exhausted without further equalization of step like metal concentration between the already doped and still undoped regions [108, 109]. Also the spectral sensitivity of the process was found even in the lower energy regions than the absorption coefficient of the chalcogenide glass. It was also argued [108, 109] that the number of $D^+$ and $D^-$ centres ($10^{17}$ to $10^{18}$ cm$^{-3}$) was smaller than the maximum number of Silver atoms ($\sim 10^{22}$ cm$^{-3}$) obtained by photo-diffusion. It was suggested [108, 109] that the light absorption occurred in the metal layer and this absorption triggered a solid state reaction at the metal semiconductor interface and it was the reaction, which pushed the doped region into the chalcogenide glass.

Yamaguchi et al in 1982 [110] proposed that the light was absorbed by the doped region and photodoping proceeds due to a light-enhanced diffusion of metal (e.g. Ag) from within doped chalcogenide glass via illumination produced defects that change places with metal atoms/ions. Therefore, maximum amount of metal diffusion depends upon the total chalcogen content. Another model proposed that diffusion of Silver occurred by an electric field generated at the interface between Silver-rich and Silver deficient regions of carriers across the interface and as Silver migrates under the influence of these electric field, the interface shifts.
Although, the photodoping of Silver has been reported in a large number of systems [110], including binary and ternary systems based on As, Te, Se, S and Se-Ge, but the models and hypotheses have been put forward mostly on the basis of properties of Ag-Se which are unlikely to be true for all systems. Therefore, investigations are necessary on electrical properties of other Silver doped (photo and thermal doped) of chalcogenide glasses.

3.1.4 Effect of Doping on \( \text{ac} \) Conductivity

By adding controlled amounts of particular impurity atoms to the chalcogenide glasses, the electrical characteristics of that semiconductor material can be favourably changed. An increase in \( \text{ac} \) conductivity is observed in amorphous semiconductors when the materials are doped with metallic impurities [119, 120]. Two types of changes are expected in \( \text{ac} \) conductivity:

(a) Uniform increase in \( \text{ac} \) conductivity over the whole frequency range, thereby preserving the \( \omega^s \) frequency dependence.

(b) Creation of a loss peak superimposed upon the background loss.

3.1.4 (a) Frequency Dependence of \( \text{ac} \) Conductivity:

If the Correlated Barrier Hopping model (CBH) mechanism involving charged structural defects is assumed to be operative for the undoped chalcogenide glasses, several consequences may result from the effect of doping. At sufficiently high concentrations, alloying effects become dominant, and as a result the bulk properties of the glasses can change. The optical gap is often significantly reduced in this way and consequently, the value of barrier height \( W_M \) for bipolaron transport would be reduced. This would give rise to an
increase in the value of ac conductivity (see section 1.2.2). A decrease in the value of frequency exponent “s” is observed because,

\[ s \equiv 1 - \frac{6kT}{W_M} \]  

(3.1)

Also, at lower concentrations, a significant interaction with charged structural defects can occur if the dopant itself is incorporated in a charged state. By the law of mass action, this may result into an increase in the concentration of defects having an opposite charge to that of dopant and, therefore, the concentration of defect states with same charge may reduce [121-123] this effect in itself could bring a change in a.c conductivity. Similarly, above a certain doping level, the Fermi energy is expected to become unpinned and move towards one of the band edges in a discontinuous fashion [124-126] which could also lead to a change in a.c conductivity.

Lots of investigations have been observed, although \( \omega^s \) frequency dependence is preserved in many of doped chalcogenide glasses [86, 127 and 128], the value of “s” varies significantly. Kitao and co-workers [86] found that in case of silver doped As\(_2\)Se\(_3\), “s” was more strongly temperature dependent when the glass was doped than when it was undoped. They fitted their results by assuming “CBH” mechanism to be operative, with single polaron hopping dominating the overall conductivity behaviour.

The necessity of assuming single polaron motion for the doped glasses imply that D\(^+\), D\(^0\) or D\(^-\), D\(^0\) centres are involved. Hirata et al [130] assumed that electrically active centres are paired. They further assumed that silver impurity forms complexes with D\(^-\) centres and that single polaron hopping occurs between D\(^+\) centres and these silver related centres. According to Elliott [129], this is not possible because such a motion of single electrons does not result into a symmetric change in the charge distribution as it does for a D\(^+\)- D\(^0\) pair, and is
unlikely to contribute significantly for the dielectric loss. One possibility is that Ag⁺ ion, acting as an ionised donor [129] to trap an electron from a neighbouring D⁺ centre, forms a D⁰ centre and a single-electron-hopping can take place between D⁺ and D⁰ centres. The maximum barrier height involved in single polaron transport is then given by \( W_M = W_2 \). It is of interest to note that the value of \( W_M \) found by Hirata et al [130] for Ag-As₂Se₃ is in good agreement with the value of \( W_2 \) quoted by Shimakawa [61] for As₂Se₃, except that, in addition, a contribution due to bipolaron CBH was found to be necessary to fit the data at lower temperatures.

Shimakawa [61] also explained the effect of impurity doping on ac conductivity using “CBH” model. But his approach is different. He assumed that silver atoms are incorporated in a negatively charged state. The law of mass action suppresses the concentration of D⁺ centres at the expense of an increase in the concentration of D⁰ centres. Single polaron transport between D⁺ and D⁰ centres is presumed to be dominant. Shimakawa assume that D⁰ centres are thermally generated and therefore their density is thermally activated.

### 3.1.4 (b) Appearance of Dielectric Loss Peak

One consequence of the incorporation of (metallic) impurities is the appearance of dielectric loss peaks, superimposed upon the background loss. Such loss peaks have been observed in Ag-doped As-Ge-Te [29 and 131] and Ni doped As₂S₃ [130], Mn doped As₂Se₃ [132]. These loss peaks occur at frequencies in the range of \( 10^3 \text{s}^{-1} < \nu < 10^6 \text{s}^{-1} \) at temperatures near ambient. The observation of loss peaks at such high frequencies is probably due to the inhomogeneous incorporation of metallic impurities, rather than to an intrinsic effect. There are two possible explanations for the Debye like loss peaks occurring in some
cases. First possibility is that electrically dominant active centres form close pairs that have single fixed relaxation time for carrier transport, thereby giving a Debye like dielectric loss peak. This is the explanation offered by Takanao et al [135] for their experimental data obtained on Mn doped a-As$_2$Se$_3$, where a simple Debye model gives very good fit to the excess ac conductivity caused by the introduction of Mn impurity. It is assumed that the background loss is due to bipolaron “CBH” in As$_2$Se$_3$ matrix. A pronounced peak is observed as a function of temperature, and the relaxation time corresponding to the peak ($\omega_c = 1$) is thermally activated, with activation energy of 0.45 eV. The second possibility for the existence of Debye like loss peak is that if there is an upper cut-off in the spatial distribution function for the intermolecular separation, a loss peak results, and the relaxation time characteristic of peak position is thermally activated, with activation energy $W_M$ [136].

3.1.5 Structure of Amorphous Arsenic Sulphide

The structures of amorphous materials are not completely different from those of the crystalline phases. The long-range order is not present in amorphous phases, while the short-range order exists and is similar to the crystalline phases. Therefore, in order to realize the properties of a-As$_2$S$_3$, the crystal structure of As$_2$S$_3$ is discussed briefly in this section.

The lattice is built up by chains of alternating S and As atoms spiralling along the c-axis (Fig. 3.3). Left and right banded chains are connected by S bridging atoms which leads to a covalently bound layer. Interlayer bonds are very weak with Vander Waals interaction. This layer structure gives flexibility to As$_2$S$_3$, and may be a key realizing the defect creation processes in the chalcogenide glasses.
3.1.6 Aim of Present work

In current study, electrical properties of a-As$_2$S$_3$ and effect of Silver (photo and thermal) doping and also Iron doping with different percentages of Iron have been investigated. Analytically, it is well studied material which has been found to have application in xerography, optical memory and threshold switching [124, 136, and 137].

Due to random arrangements of atoms, the amorphous semiconductors have a system of high complexities. Accordingly, the investigation of their properties requires a large number of parameters. Eventually, the experimentalists find serious problem in measurements, justification and characterization of these materials.
Keeping these points in view, it becomes necessary to study their different properties. The present work is an attempt in that way.

3.2 DC AND AC CONDUCTIVITY OF Ag$_2$As$_2$S$_3$

3.2.1 DC Conductivity

The temperature dependence of dc conductivity of Silver doped As$_2$S$_3$ has been shown in Figure 3.4.

It is evident from the figure that Ag-As$_2$S$_3$ glasses indicate a temperature activated behaviour and follow the relation:

$$\sigma = \sigma_0 \exp \left(-\frac{\Delta E_a}{kT}\right)$$  \hspace{1cm} (3.2)

![Graph of Log dc Conductivity versus 1000/T, for Undoped, Thermaldoped and Photodoped Ag$_2$As$_2$S$_3$.](image)

*Fig. 3.4, Log of dc Conductivity versus 1000/T, for Undoped, Thermaldoped and Photodoped Ag$_2$As$_2$S$_3$.***
It is also clear from the figure that $\Delta E$ increases with Ag doping in the studied temperature range. Table 3.1 shows the activation energy for undoped, thermaldoped and photodoped $\text{As}_2\text{S}_3$ which increases from 0.87 eV for undoped to 0.88 eV for thermaldoped and to 1.00 eV for photodoped samples. Interestingly dc conductivity increases for thermal doped and photodoped samples.

**Table 3.1**

Experimental values of dc Activation Energy ($\Delta E$) for Iron Doped $\text{As}_2\text{S}_3$

<table>
<thead>
<tr>
<th>GLASS</th>
<th>DC ACTIVATION ENERGY($\Delta E$) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{As}_2\text{S}_3$</td>
<td>0.87</td>
</tr>
<tr>
<td>Ag-$\text{As}_2\text{S}_3$</td>
<td>0.88</td>
</tr>
<tr>
<td>Thermal doped</td>
<td></td>
</tr>
<tr>
<td>Ag-$\text{As}_2\text{S}_3$</td>
<td>1.00</td>
</tr>
<tr>
<td>Photodoped</td>
<td></td>
</tr>
</tbody>
</table>

**3.2.2 Frequency Dependence of ac Conductivity**

The results of the ac conductivity ($\sigma_{ac}$) for Ag-$\text{As}_2\text{S}_3$ system at different temperatures and frequencies have been shown in different figures as below.
Figures 3.5, 3.6 and 3.7 show the frequency dependence of the measured conductivity for undoped, photodoped and thermaldoped samples respectively at different temperatures.

From these figures it is clear that $\sigma_{ac} = A\omega^s$ (1.5). Where “$s$” is frequency exponent and “$A$” is a constant.

Figures show that slope of the curves decreases with increasing temperature for all samples. This clearly indicates that value of “$s$” decreases with increasing temperature.

*Fig. 3.5, Log of ac Conductivity versus log of Frequency at different temperatures for Undoped Arsenic Sulphide.*
Fig. 3.6, Log of Frequency versus log of Conductivity at different temperature for **Thermaldoped Arsenic Sulphide**.

Fig. 3.7, Log of Conductivity versus log of Frequency at different temperatures for **Photodoped Arsenic Sulphide**.
3.2.3 Temperature Dependence of ac Conductivity

Figures 3.8, 3.9 and 3.10 show, temperature dependence of conductivity (ac and dc) for undoped, thermaldoped and photodoped samples. The experimental results indicate that ac conductivity dominates over dc conductivity at lower temperatures. However, dc conductivity follows band conduction mechanism and dominates over ac conductivity in the higher temperature range (particularly in case of doped As$_2$S$_3$).

Fig. 3.11 shows the temperature dependence of frequency exponent “s” for all the samples. Figure indicates that value of “s” decreases with increasing the temperature, but increases with doping at the same temperature.

![Fig. 3.8, Log of Conductivity versus 1000/T for Undoped Arsenic Sulphide at different frequencies.](image-url)
Fig. 3.9, Log of Conductivity versus 1000/T for Thermaldoped Arsenic Sulphide at different frequencies.

Fig. 3.10, Log of Conductivity versus 1000/T for Photodoped Arsenic Sulphide at different frequencies.
However it has been observed that in case of thermal doping, if the doping temperature is increased, the value of “s” also increases (Fig. 3.12).

Fig. 3.13 (a, b, c & d) shows the frequency dependence of dielectric constant “k” at the four different temperatures for undoped, photodoped, and thermaldoped As₂S₃. Figures clearly indicate that at lower temperatures, the dielectric constant is same for photodoped and undoped As₂S₃ whereas it is higher for thermal-doped As₂S₃.
Fig. 3.12, Temperature dependence of frequency exponent “s” for Thermaldoped Ag–As$_2$S$_3$ (doping temperature being different).
Fig. 3.13, Frequency dependence of dielectric constant “k” for Undoped, Photodoped and Thermaldoped samples at (a) 273K, (b) 283K, (c) 313K and (d) 323K.
However, at higher temperatures the value of dielectric constant is maximum for photodoped As$_2$S$_3$, whereas the value of dielectric constant “k” for undoped As$_2$S$_3$ does not vary much with temperature.

Figure 3.12 (a, b & c) shows the temperature dependence of ac conductivity for all samples of As$_2$S$_3$ at 2 KHz, 10 KHz and 50 KHz. Figures indicate that for undoped sample, conductivity is not changing much with temperature. However, in case of Ag-doped samples, the ac conductivity shows a sharp jump in the conductivity at around 283K. It is also clear from figures that ac conductivity of As$_2$S$_3$ decreases on doping, particularly in the lower temperature range. Figures show that the fall in conductivity, because of doping is maximum for photodoped As$_2$S$_3$ at lower temperatures.

Figure 3.13 (a, b) shows the temperature dependence of dielectric constant “k” at two different frequencies (2 KHz and 50 KHz). The figures indicate that at lower temperatures the value of “k” for undoped and photodoped sample is nearly constant, whereas it is slightly more for thermaldoped sample. However at about 283K, the value of “k” suddenly increases for thermaldoped sample and at about 293K there is a jump in the value of “k” for photodoped sample. This jump in the value of dielectric constant “k” is more for photodoped samples than that of thermaldoped samples.
3.2.4 Discussion

The above results can be easily explained using a modified Correlated Barrier Hopping Model (CBH). It has been established that the dissolution of silver into chalcogenide involves the migration of Ag⁺ ions and electrons. We have large number of D⁺, D⁻ and unsaturated D⁰ defect sites in chalcogenides. A new equilibrium is expected after the migration of Ag⁺ and electrons, i.e.

\[ D^- + Ag^+ \rightarrow [(D^-)(Ag^+)]^0 = [(As_2S_3)-(Ag^+)]^0 \]  \hspace{1cm} (3.4)

And

\[ D^0 + e^- \rightarrow D^- \]  \hspace{1cm} (3.5)
Fig. 3.15, Temperature versus Dielectric constant for Undoped, Photo doped and Thermal doped samples at (a) 2 kHz, and (b) 50 kHz.
These reactions suggest that, on doping, the concentration of $D^o$ centres decreases. According to Correlated Barrier Hopping model ac conductivity is proportional to $R^6$ (where $R$ is the hopping distance) (equation 1.39). Now hopping distance “$R$” is inversely proportional to $W$ (taken as $W_1$ for hopping between $D^o$ and $D^+$) (equation 1.38).

Total conductivity is the combined mechanism of three hopping processes. These processes are bipolaron hopping between $D^+$ and $D^-$ centres, single polaron hopping between $D^o$ and $D^-$ centres, and $D^o$ and $D^+$ centres. Also $W$ is equal to $W_m$, which is slightly less than band-gap for bipolaron hopping, whereas, it is equal to $W_1$ and $W_2$ for two types of single-polaron hopping, which are substantially less than $W_m$ for bipolaron hopping.

The smaller values of $W_1$ and $W_2$ for single polaron hopping means, that value of $R_w$ is much more for single polaron hopping as compared to bipolaron hopping as per equation (1.39), which in turn means that the contribution of each $D^o$ centres to conductivity is much more than $D^+$ or $D^-$ centre. Therefore, the reduction in $D^o$ centres causes a decrease in the value of conductivity at lower temperatures as has been observed in fig. 3.14 (a, b & c).

The neutral dipolar states $[D^+Ag^+]^o$ are expected to interact with each other, thereby forming long dipolar chains. These dipolar chains do not contribute to conductivity at lower temperatures. Figure 3.15 shows that at lower temperature the dielectric constant is almost same for pure $As_2S_3$, and optically doped Ag-$As_2S_3$, thereby, indicating that the dipolar states $Ag^+-D^-$ do not contribute towards dielectric constant, however a higher value of dielectric constant at lower temperatures for thermal-doped Ag-$As_2S_3$ indicates that, some of these dipolar states $[Ag^+-D^+]$ may be non-interacting (not being part of long dipolar chains) and thereby, contributing to dielectric constant. However at
higher temperatures, dielectric constant is more than undoped As$_2$S$_3$
for both thermaldoped Ag-As$_2$S$_3$ and optically doped Ag-As$_2$S$_3$. This
indicates that at higher temperatures these dipolar chains break down
and start contributing towards increased capacitance/dielectric
constant.

A jump in the value of conductivity and dielectric constant for
doped As$_2$S$_3$ at higher temperatures as per Figs. 3.14 and 3.15 can be
also attributed to breakage of dipolar chains. A jump in the dielectric
constant of optically doped Ag-As$_2$S$_3$, which has been observed at
higher temperatures than that of thermaldoped Ag-As$_2$S$_3$ is also
indicative of the fact that interaction of dipolar states is stronger for
optically doped Ag-As$_2$S$_3$ and therefore requires higher energy for
breaking-down.

### 3.3 DC AND AC CONDUCTIVITY OF Fe-As$_2$S$_3$

#### 3.3.1 Preparation of Materials and Samples

Thermal quenching method has been used to prepare Fe-As$_2$S$_3$
because it is one of the best methods to obtain a good glassy material
with good structural and compositional uniformities.

In some stable glasses e.g. As$_2$S$_3$ and As$_2$Se$_3$, the crystallization
process is so slow that glassy state can be obtained even by cooling
the melt slowly whereas in some unstable glasses e.g. As-Te and some
“Ge” containing glasses a fast cooling becomes necessary to obtain
the glassy state. Moreover, in some systems, the glassy state may exist
for a few compositions e.g. As-Te is glassy only for the composition
As$_{50}$Te$_{50}$ and As$_{60}$Te$_{40}$ while for other atomic percentages it is either
crystalline or partly crystalline.
For the present work, As$_2$S$_3$ glasses having different percentages of Iron (Fe) have been used. The doped materials (Fe-As$_2$S$_3$) have been prepared by heating it in a Rocking Furnace (Fig. 3.16). The desired quantities of materials having 99.999% purity were weighed and sealed in a quartz ampoule under a pressure of $10^{-5}$ torr. This ampoule is then mounted on a rocking arrangement and subjected to heat treatment in a furnace. The temperature of the furnace is initially raised to the melting point of the constituent elements and maintained at this temperature for 36 hours. During this process of heating, the ampoule is continuously rocked (vibrated) to make sure that the homogeneity of the melt is obtained and to prevent the growth of micro crystalline structure. The ampoule is dropped into liquid nitrogen to quench the homogeneous melt.

*Fig. 3.16, Rocking Furnace for the preparation of Glassy alloys.*
The solidified semiconducting alloy of Fe-As$_2$S$_3$ is then taken out by breaking open the ampoule. X-ray diffraction study was then performed to check the amorphous nature of the material so prepared. It is an important part of the experiment because it can affect the results that differ only due to different types of samples. Thin compressed circular pellets have been made by finely grinding the material and then compressing the powder to maximum compaction in a die under hydraulic pressure (~ 10$^6$Kg/m$^2$), so that no voids are left in the sample. The amount of pressure required depends on the size of the sample and nature of the material. The samples are then annealed at a temperature of ~ 339 K for about 24 hours. The faces of the annealed pellets were coated with aquadag (a conducting carbon emulsion) for conductivity measurements.

3.3.2 DC Conductivity

Generally, in most of the chalcogenide glasses, the dc conductivity is a linear function of 1/T and near room temperature it has an Arrhenius type of temperature variation, e.g.

$$\sigma_{dc} = C \exp (-\Delta E_0/kT)$$ \hspace{1cm} (3.6)

Where “$\Delta E$” and “k” are the activation energy of dc conductivity and the Boltzman Constant respectively and the value of “C” lies in the range of $10^3$-$10^4$ $\Omega^{-1}$cm$^{-1}$ [30].

The Measurements of dc conductivity have been carried out using a digital Pico-ammeter (model DPM-111). The instrument can measure the low dc currents from 1 Pico ampere to 100 Nano amperes, within accuracy of ± 0.25% for all ranges, which for ease; readings are directly obtained on a 3½ digit LED display.

Log $\sigma_{dc}$ against 1000/T curves have been plotted (Fig. 3.17) to obtain the activation energy ($\Delta E_0$) for Iron doped As$_2$S$_3$ samples in...
various concentrations of Fe (0.0%, 0.4% and 1.0%). The results show a change in activation energy from 0.73 eV to 1.03 eV.

From the figures it is evidence that for all samples log of σdc is a straight line. It is also evidence from the figure that ΔE0 decreases for 0.4 % Iron doping. However, with 1.0 %Fe doping ΔE0 increases but the dc conductivity decreases.

![Graph](image)

**Fig. 3.17, Log of dc Conductivity versus 1000/T, for different percentages of Iron doped As2S3.**

### 3.3.3 Frequency Dependence of ac Conductivity

Measurements of ac conductivity for Fe-As2S3 system at different temperatures and frequencies (Figures 3.18, and 3.19) show that for all these glasses, σac follows the relation 3.3.

The decrease in slope with increasing temperature indicates that the value of frequency exponent “s” decreases with increasing temperature.
**Table 3.2**

Experimental values of dc Activation Energy (ΔE) for Iron Doped As$_2$S$_3$

<table>
<thead>
<tr>
<th>GLASS</th>
<th>DC ACTIVATION ENERGY (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$_2$S$_3$</td>
<td>0.87</td>
</tr>
<tr>
<td>0.4%Fe-As$_2$S$_3$</td>
<td>0.73</td>
</tr>
<tr>
<td>1%Fe-As$_2$S$_3$</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*Fig. 3.18, Frequency dependence of ac Conductivity at different temperatures for 1.0% Fe-As$_2$S$_3$.***

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3.3.4 Temperature Dependence of ac Conductivity

Figure 3.20 shows the temperature dependence of frequency exponent “s” for different percentages of Iron in As₂S₃. The decrease in slope with increasing temperature clearly indicates that the value of “s” decreases with increasing temperature in all concentrations of Fe. Besides that the value of “s” also decreases with increasing the percentage of Fe doping.

The result of measurements of log ac conductivity vs. 1000/T for Iron doped Arsenic Sulphide having different concentration of Iron, \((\text{As}_2\text{S}_3)_{100-x}\text{Fe}_x\) (x = 0.0, 0.4 and 1.0) at different frequencies are shown in figure 3.21 (a, b and c). The figure shows that ac conductivity decreases with decreasing temperature. Moreover, ac conductivity decreases with increase in the concentration of Fe.
Fig. 3.20. Temperature dependence of frequency exponent $"s"$ for different percentages of Fe in Fe-As$_2$S$_3$ system.
\[ \log(\sigma_{ac} / \Omega^{-1} \text{cm}^{-1}) \]

(a) \[ 1 \text{KHz} \]
- 0.0\% Fe
- 0.4\% Fe
- 1.0\% Fe

(b) \[ 2 \text{KHz} \]
- 0.0\% Fe
- 0.4\% Fe
- 1.0\% Fe

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Fig. 3.21, Temperature dependence of ac Conductivity for different concentrations of Fe in Fe-As$_2$S$_3$ system at (a) 1 KHz, (b) 2 KHz and (c) 10 KHz.

3.3.5 Discussion

The most widely accepted model to describe the conductivity behaviour of amorphous semiconductor is Correlated Barrier Hopping model (CBH). Therefore, this model has been used to explain the behaviour of Iron doped Arsenic Sulphide glass. The values of maximum barrier height $W_M$ and other parameters like $W_1$, $W_2$, $U_{eff}$, and “k” (dielectric constant) have been estimated from the behaviour of the temperature dependence of ac conductivity for pure and Iron doped As$_2$S$_3$. The sensitivity of ac conductivity w.r.t. temperature increases with doping. Moreover, it is also clear from figure 3.20 the
value of frequency exponent “s” decreases with increase in Iron content.

Both these observations point out that the value of maximum barrier height “$W_M$” decreases with increase in Fe content. As discussed earlier (section 1.2.2 and section 3.3), if ac conductivity decreases, the decrease in the value of “$W_M$” can only be explained by a sharp decrease in the number of defect states.

Based upon these observations, different values of parameters were tried and the best fits for the ac conductivity were obtained using Correlated Barrier Hopping model “CBH” (equation 1.37). The values of parameters used for the calculation are given in table 3.3.

Figs. 3.22, 3.23 and 3.24 show the temperature dependence ac conductivity behaviour of $\text{As}_2\text{S}_3$, ($\text{As}_2\text{S}_3)_{99.6}\text{Fe}_{0.4}$ and ($\text{As}_2\text{S}_3)_{96.0}\text{Fe}_{1.0}$ for different frequencies along with the theoretically calculated values.

### Table 3.3
Parameters used for CBH Model Fitting for Undoped and Iron-doped Arsenic Sulphide.

<table>
<thead>
<tr>
<th>GLASS</th>
<th>$W_M$ (eV)</th>
<th>$W_1$ (eV)</th>
<th>$W_2$ (eV)</th>
<th>$U_{\text{eff}}$ (eV)</th>
<th>$N_T$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{As}_2\text{S}_3$</td>
<td>2.10</td>
<td>0.80</td>
<td>0.85</td>
<td>0.45</td>
<td>2.00E19</td>
</tr>
<tr>
<td>($\text{As}<em>2\text{S}<em>3)</em>{99.6}\text{Fe}</em>{0.4}$</td>
<td>2.00</td>
<td>0.75</td>
<td>0.85</td>
<td>0.40</td>
<td>1.30E19</td>
</tr>
<tr>
<td>($\text{As}<em>2\text{S}<em>3)</em>{96.0}\text{Fe}</em>{1.0}$</td>
<td>1.95</td>
<td>0.80</td>
<td>0.75</td>
<td>0.40</td>
<td>9.10E18</td>
</tr>
</tbody>
</table>
Fig. 3.22. Temperature dependence of ac Conductivity for Experimental and Theoretical Undoped As$_2$S$_3$ at (a) 5 KHz, (b) 10 KHz and (c) 20 KHz.
Fig. 3.23, Temperature dependence of ac Conductivity for Experimental and Theoretical (As$_2$S$_3$)$_{9.6}$ Fe$_{0.4}$ at (a) 2 KHz, (b) 5 KHz and (c) 10 KHz.
Fig. 3.24, Temperature dependence of ac Conductivity for Experimental and Theoretical $(\text{As}_2\text{S}_3)_{99}\text{Fe}_{1.0}$ at (a) 5 KHz, (b) 10 KHz and (c) 20 KHz.
It is clear from the figures that a good match of the experimental values and theoretical values is available.

From table 3.3, it is evident that Iron doping leads to the change in behaviour from p-type conductivity \((W_1 < W_2)\) to n-type conductivity \((W_1 > W_2)\). The decrease in the value of density of states is also predicted by the experimental values as is evident from the table.

The decrease in ac conductivity with doping can also be explained using 8-N rule given by Mott [140]. The theory also points out the decrease in the number of defect states.