Chapter 1

Introduction

The potential importance of the transition metal doped semiconductors i.e. dilute magnetic semiconductors, both in terms of fundamental as well as technological views are described in detail. The carried out studies are Fe (0.01) doped Ge$_{1-x}$Sb$_x$ films, Fe (0.008) doped Sb$_{1-x}$Se$_x$ films, In$_{1-x}$Fe$_x$Sb (x = 5, 10 and 20 %) bulk system and transition metal (Fe, Co, Mn and Ni) doped InSb films respectively. The study will throw light on understanding the structural, electrical, surface morphological and magnetic properties of materials. Following a brief literature survey on these materials, few of the unsolved/controversial issues concerning the various properties of these materials are described. The transport properties of semiconductors are also explained. At the end the motivation of the present work is presented.
1.1 Introduction

The outstanding feats in the field of microelectronics and information technology have had an enormous impact on our daily life and have changed the style of living all over the world. Whenever people use data processing devices like computers, to facilitate their work, they are basically using the properties of electron charge and spin. Microelectronic devices and circuits are invented for data processing by manipulating the electron charge as well as spin. These microelectronic devices made from elemental and compound semiconductors explore the charge carriers for modifying electronic and optical properties. But they are nonmagnetic in nature. The spin characteristics of the electrons are not studied.

Extensive studies on miniaturization of devices have been done by changing the surface to volume ratio of materials from microscopic to Nano scale regime. This change in the fabrication of devices has definitely enhanced the charge behavior in the material. However, the study that includes both the behavior of spin along with charge property of devices is created special interest in the field of science and technology. Such devices developed, based on spin based electronics are now known as Spintronics. These Spintronics materials possess electronic as well as magnetic properties.

Generating a spin polarized current, by manipulating spin states and sensing the polarization are basic requirements for the realization of spintronics technology. One of the methods to generate a spin polarized current is to run the current through a ferromagnetic material. The key elements of spintronics are injection, manipulation, transfer and detection (i.e. how the spin is created or destroyed and moves in metal and semiconductor) of spin-polarized carriers across a semiconductor device. Ferromagnetic materials can function as a spin supplier and injector. However, the
spin injection efficiencies of ferromagnetic metals in a semiconductor of the order of 1%, which appears to be very less [1]. This low spin injection efficiency is due to the conductivity mismatch at the metal-semiconductor interface. The advances in material science have led to the development of ferromagnetic semiconductors which are believed to have better injection efficiency.

The general interest in these ferromagnetic semiconductors and semimetals are due to their larger spin-flip length, which is favorable for laterally patterned spin devices. The first generation materials are Europium (Eu) chalcogenides [2] and multinary chalcogenides of Chromium (Cr) [3], which are studied intensively in the late 60’s and early 70’s. These multinary chalcogenides with spinel structures, such as CdCr$_2$Se$_4$, are the most extensively studied magnetic semiconductor [4-7]. Chemical vapor transport using halogen or halides as transporting agents is also one of the techniques for bulk crystal growth of chalcogenide spinels [8-9]. On the other hand, Europium mono-chalcogenides EuX (X = O, S, Se and Te) crystallize in a NaCl-type F.C.C. structure. EuO and EuS compounds show ferromagnetism with 68 K and 16.2 K Curie temperature respectively [10-12]. EuSe is metamagnetic whereas EuTe exists in antiferromagnetic state [13]. Due to melting point higher than 2000 °C, growth of Europium chalcogenides from the melt is quite difficult. e.g. EuS single crystals are grown by a normal freezing technique using a high-pressure furnace, in which the temperature is raised above 2500 °C. Good quality single crystals of several millimeters in size are cleaved out from the ingot. Moreover, CrBr$_3$, transition metal, rare earth oxides, fluorides, phosphides and few other ferromagnetic semiconductors such as BiMnO$_3$, MSeO$_3$ and MTeO$_3$ (M = Mg, Mn, Co, Ni, Cu, and Zn) [14-16] also belong to the same generation of magnetic semiconductors. Interesting change in physical properties of these magnetic semiconductors observed are magnetic red shifts.
of the absorption edge and large negative magneto-resistance (MR) [17-18]. However, researcher, lost interest in these materials due to their low Curie temperatures, which are far below the room temperature (RT) and the growth of good quality single crystals are very difficult. After that, a lot of theoretical and experimental efforts focus on the new class of semiconductors which has some unique properties that enhance their potential towards the development of optoelectronic device. The researchers tried to understand the underlying physics of the unusual phenomenon associated with these specific semiconductors. In 1977, Komarov et. al. [19] first reported the giant enhancement of magnetic-optical effects in CdMnTe. That is the birth of magnetic semiconductors, called Dilute Magnetic Semiconductors (DMS). These materials are particularly important due to their capability to accommodate a high percentage of Mn atoms (as high as 77 %) and its appropriate energy gap for optical application.

Antimony (Sb) is a group V semimetal having a rhombohedral structure with electronegativity of 2.05. The extensive investigations have been made both from the experimental and theoretical point of view on the electronic and magnetic properties of this semimetals.

It is also known that the addition of small quantities of magnetic impurities [20-22] into the semimetals can produce a small band gap. Somayajulu et. al. [23] observed that in addition of 0.8 % Fe into Sb semimetal produced a band gap of 0.08 eV and band gap extended up to 0.18 eV on bringing Selenium concentration of only 3 % (Fe_{0.008}Sb_{1-x}Se_{x}) into the system. Hall measurement shows that bringing Se in to the system, makes it an n-type semiconducting nature and charge carrier densities increased from \(4.2 \times 10^{19}\) cm\(^{-3}\) to \(1.142 \times 10^{21}\) cm\(^{-3}\) for \(x = 0.01\) to \(0.10\) in Fe_{0.008}Sb_{1-x}Se_{x} bulk alloy. As this system was not conventional compound semiconductor it was named as dilute magnetic semiconducting alloy (DMSA).
The active research on DMS started after the development of III-V based diluted compound semiconductors, in which magnetic properties have been found to be strongly dependent on the carrier concentration in the materials [24-27].

1.2 Dilute Magnetic Semiconductors (DMSs)

The DMS materials are conventional semiconductors, in which appropriate fraction of the original atoms is substituted by elements which are capable to introduce the localized magnetic moment. These materials are commonly known as dilute magnetic semiconductors (DMSs). Due to this substitution, these materials not only retain the semiconducting properties, but can also possess magnetic properties. The most common DMS’s are IV group (e.g. Si$_{1-x}$Mn$_x$ [28], Ge$_{1-x}$Cr$_x$ [29], Ge$_{1-x}$Mn$_x$ [30]), III-V group (e.g. GeTe [31], In$_{1-x}$Mn$_x$Sb [32]), II-VI group (e.g. Zn$_{1-x}$Fe$_x$O [33], Zn$_{1-x}$Mn$_x$O [34-35]), IV-VI group (e.g. Ge$_{1-x}$Mn$_x$Te [36], Ge$_{1-x}$Cr$_x$Te [37]) etc. The rare earth elements (e.g. Eu, Er, Gd) are also used as magnetic atoms in DMS [10-12]. In general DMS can be expressed in many different ways, such as A$_{1-x}$M$_x$B, AB(M) or (AB)$_{1-x}$(MB)$_x$. Here x indicates the fraction of the non-magnetic cations (A) of the semiconductor AB, which is randomly replaced by magnetic 3d or 4f ions (M). DMS alloy is another class of material which is a mixture of ordinary and magnetic semiconductors. In DMS alloys as lattice parameters, energy gap and other band parameters can be tuned between the values applicable to the primary semiconductors AB and MB by varying the value of x, like as II–VI semiconductor ternary of Cd$_{1-x}$Zn$_x$S, Cd$_{1-x}$Mn$_x$S, Zn$_x$Mg$_{1-x}$O, and CdS$_{1-x}$Se$_x$ with continuously tuned band gap [38-42].

It is very important to choose a suitable semiconductor material for DMS system because the properties and compositions of host material influence the properties of resultant DMS material.
1.3 Transport phenomenon in semiconductors

In the second half of the 1940’s, Bardeen, Brattain and Shockley discovered the transistor effect, after the discovery of this effect, a breakthrough in the low temperature conductivity is seen in doped Germanium. In 1956 Conwell [43] and Mott [44] suggested a model for the new process of conduction, in which charge carriers conduct the electric current by thermally activated tunneling from an occupied site to an empty site. This process is known as “Phonon Assisted Hopping”. It is the starting point of a number of transport theories, such as the model of Miller and Abrahams [45]. This model became the most widely accepted theory of conduction between localized states and is the source of the Variable Range Hopping (VRH) theory of Mott [46].

According to this model, electrons hop from an initial state suppose ‘i’ to another state ‘j’ with lowest energy possible. For such an energy the site ‘j’ is statistically located from ‘i’, involving a distance $r_{ij} = R$, which generally is much larger than the decay length of the wave function. According to Mott, the conductivity ‘$\sigma$’ depends on two factors (i) Boltzmann factor $\exp(-W/kT)$ and (ii) overlap of the functions $\exp(-2\alpha R)$, where

- $K$ - Boltzmann constant
- $T$ - Temperature
- $W$ - Hopping Energy
- $\alpha^{-1}$ - wave function decay length
- $R$ - Distance separating sites ‘i’ and ‘j’

Mott considered that the conductivity “$\sigma$” behaves as the factor $\exp(-2\alpha R - W/(kT))$ so it can be written as
\[ \sigma = \sigma_0 \exp(-2\alpha R - \frac{W}{kT}) \]  \hspace{1cm} (1.1)

Here \( \sigma_0 \) is a factor that is weakly temperature dependent. The idea of Mott is to maximize the hopping probability.

So the expression for the hopping energy \( W \) may be written as

\[ W = \frac{3}{4\pi R^3 N(E_F)} \]  \hspace{1cm} (1.2)

This gives the minimum rate of “R” as

\[ R_{3D} = \frac{3^{1/2}}{[8\pi\alpha N(E_F)k]^{1/4} T^{1/4}} \]  \hspace{1cm} (1.3)

Where \( N(E_F) \) is the density of states at the Fermi level. It then appears that the distance of a hop increases as \( T \) decrease. Substituting equation (1.2) and equation (1.3) into equation (1.1) we get \([T^{1/4}]\) Mott conductivity for noncrystalline semiconductor as

\[ \sigma_{3D} = \sigma_{3D}^0 \exp \left[ -\left( \frac{T_{3D}^0}{T} \right)^{1/4} \right] \]  \hspace{1cm} (1.4)

This mechanism is a powerful tool to explain and characterize electrical transport properties in semiconductors. But not all semiconductors can be fitted by this model. The Granular metal mechanism is just an example of various mechanisms that have been proposed as an alternative to VRH theory. In many cases the transport properties measured showed a different transport mechanism, thus different models can be applied at a different temperature range, which proves that the transport in a semiconductor is a complicated phenomenon.
1.4 Ion Beam Irradiation

The study of the Swift Heavy Ion (SHI) irradiation is an important technique to create controlled defects (via point, cluster and columnar) and modify the strain and transform the phase in the thin films. It is an established fact that SHI irradiation is responsible for the substantial changes in the transport, surface morphology and magnetic properties of thin films because it creates magnetic anisotropy, defect formation, amorphization of the material etc. Figure 1.1 demonstrates the schematic diagram, showing the principle of acceleration of ions used in 15 UD pelletron at IUAC, New Delhi.

The 15 UD Pelletron accelerator is a versatile, tandem type electrostatic accelerator. In this accelerator, negative ions are produced using Cesium ion sputtering known as SNICS (Source of Negative Ion by Cesium Sputtering). The pre-accelerated ions are injected into an accelerator tank which is filled with high insulating sulfur hexafluoride gas (SF₆) at 7 atmospheric pressure. The injector magnet is used for selection of ion beam by mass spectroscopy. After selection of ions as per requirement, the ions pass through accelerating tubes from the column top of the tank to the positive terminal and get accelerated. On reaching the terminal, they pass through the stripper foils, which removes electron from the negative ions and transforms the negative ion into the positive ions with high charge state. Finally, switching magnet diverts the high energy ion beam into the selected beam line of the beam hall and quadruple magnets are used to focus the beam. The positive ions are accelerated towards ground potential to bottom of the tank [47].
Fig. 1.1: A schematic diagram showing the principle of acceleration of ions used in pelletron at IUAC, New Delhi

The energy of the ions coming from the accelerator is given by

$$E_i = E_{decpot}(1+q)V$$ \hspace{1cm} (1.5)

where $E_i$ is the energy of ions with charge state $q$, $V$ is the terminal potential in MV and $E_{decpot}$ is the deck potential of the SNICS source.

### 1.4.1 Interactions of ions with matter

When an energetic ion passes through the material, the energy is transferred from the energetic ion to the lattice of the target material mainly via two processes (i) nuclear energy loss and (ii) electronic energy loss. In nuclear energy loss $\left(\frac{dE}{dx}\right)_n$ or $S_n$, elastic collision with target atoms leads to displacement of atoms from their regular lattice site while inelastic collision between heavy ions and target electrons, rise their excitation or ionization in electronic energy loss $\left(\frac{dE}{dx}\right)_e$ or $S_e$.

It is known that when SHI pass through materials, it creates cylindrical zones at a Nano level in the materials. For the case of higher energy ion irradiation, $S_e$ is
There are several reports on the electronic energy loss, inside the materials, creating structural modifications which can be understood by two basic models named as (1) Thermal Spike model (2) Coulomb Explosion model.

1.4.1.1 Thermal spike model

In the thermal spike model the energy transfer from the bombarding of SHI to the lattice is a two-step thermodynamic process. First one is the evolution of the energy within the target electron via electron-electron interaction and the second one is transfer of energy between electron and lattice atom via electron (phonon coupling). This energy transfer leads to increase in local temperature that can reach the melting temperature of the material resulting in the formation of highly disordered state or amorphization. Ultrafast quenching of the molten matter takes place. According to this model, the energy transfer through electron-electron interaction takes approx. $\sim 10^{-14} - 10^{-13}$ sec while energy transfer through electron phonon coupling takes place with in $\sim 10^{-12}$ sec.

1.4.1.2 Coulomb Explosion Model

According to this model, the incoming ions deposit their energy onto the target electrons. The electrons are then ionized, leaving behind a cylindrical zone of ionized cores, which creates coulomb repulsion, leading to the explosion of the ions. In this model the formation of tracks can be determined using different criteria [48].

1. The local electrostatic stress developed in the depleted region should overcome the local mechanical strength or the bonding strength, therefore the track formation is possible in material having properties such as, low dielectric constant, close spacing and low mechanical strength.
2. For continuous tracks, there should be one ionization per atomic plane crossed by the incident charged particle.

3. Track formation is not possible for material having a high free electron density. According to this model, electrons ejected by the charged particle are replaced by the free electrons in the material before the depleted region explodes.

4. Since the ionized region has a high concentration of holes, these holes might move apart and permanently suppress the track formation.

**1.5 Energy loss Mechanism**

In 1911 Ernest Rutherford performed an experiment with interaction of charge particle scattering by solids. By this principle when ions traverse through solid matter, they ionize the atoms or molecules on interaction. Both the charge particle electron and positive ions lose their own energy while passing through the matter. The energy of these charged particles per unit length is known as “stopping power” and written as-

\[ S(E) = -\frac{dE}{dx} \]

Here \( E \) denotes the energy and \( x \) is denoted by the path length.

The numerical value of the stopping power is positive and minus sign denotes the loss of energy of the ions/electrons as the length increases. The stopping power is the material dependent. The energy loss also can be expressed in terms of Linear Energy Transfer (LET). It’s a measure of energy deposited per unit ion path length, having SI unit eV/m. The magnitude of ionization depends upon the deposited energy along the ion track or LET [49].

**1.5.1 Electronic and Nuclear Energy loss**

The stopping power or energy loss depends on the properties of target material & type and energy of the particle.
1.5.1.1 Electronic Energy loss

In electronic stopping the ions slow down due to the inelastic collision between bound electrons in the medium. The term inelastic is used to signify that the collisions may result in both excitations of bound electrons of the medium and in excitations of the electron cloud of the impinging ion.

It is very difficult to describe every possible interaction for all possible ion charge states. While the electronic stopping power is often described as a simple function of energy $S_e(E)$ which is an average taken over all energy loss processes for different charge states. At energies which is lower than about 100 KeV per nucleon, it becomes more difficult to determine the electronic stopping power theoretically.

![Figure 1.2: Comparison of electronic and nuclear energy stopping at different energy range](image)

1.5.1.2 Nuclear energy loss:

From nuclear stopping, ions lose their energy by elastic collisions between the ion and atoms in the sample. If one knows the form of the repulsive potential $V(r)$ between two atoms is known, it is possible to calculate the nuclear stopping power $S_n(E)$. Nuclear stopping increases with the mass of the ion. As shown in figure 1.2, nuclear stopping is larger than electronic stopping at the lower range. For very light ions slowing down in heavy materials, the nuclear stopping is weaker than the
electronic stopping at all energies.

At intermediate energies, the stopping power is therefore the sum of two terms.

\[ S(E) = S_e(E) + S_n(E) \]

As shown in figure 1.3 at the beginning of the slowing down process at high energies, the ion slows down mainly by electronic stopping and it moves almost in a straight path. When the ions are slowed down sufficiently, the collisions due to nuclear stopping becomes dominant. The atoms of target material receive enough energy from incident ions to recoil and get displaced from lattice positions.

**Figure 1.3: Interaction of ion beam with target material**

These collision cascades are the main cause of defects during ion implantation in materials (metals and semiconductors). Figure 1.3 shows a typical range distribution of ion energy deposited in the solid [50].
1.6 Motivation

Significant efforts to study the electronic and magnetic properties of various DMS compounds started in late 1980s [51]. But, the real interest on DMS arose when Ohno et. al. [24-27] successfully developed Mn-doped GaAs and InAs ferromagnetic semiconductors with doping concentration $x = 1$-$10\%$ using Low Temperature-Molecular Beam Epitaxy (LT-MBE) technique. The discovery of ferromagnetism in (GaMn)As with $T_c = 110$ K, caught the attention of the researchers in transition metal (TM) based DMSs [52]. The research on DMSs is concentrated on three major fronts: (i) the microscopic origin and fundamental physics of the ferromagnetism that occurs in these systems (ii) the growth and engineering of these materials including defects and (iii) the development of spintronic devices with new functionalities. Furthermore, the magnetic and electronic properties of the DMS system depend on the distribution of dopants and on the local environment. The present work on the thin films is motivated by ferromagnetic ordering seen in Fe doped V-VI (Sb$_{1-x}$Se$_x$) alloy [23], Ge$_{1-x}$M$_x$ (where M is V and VI group dopants) [53] and transition metal doped InSb alloy [54] in bulk semiconductors. But for all practical purpose thin films are desirable. Hence, thin films of these materials along with other bulk materials are prepared using thermal evaporation technique. Various studies such as structural, electrical, surface morphological and magnetic properties of these thin films will be discussed.
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