Chapter 6

Conclusion and Future outlook

In this chapter all the results are summarized and the work to be carried out in future is presented.

This thesis work deals with the investigation of structural, electrical, surface morphological and magnetic properties of some dilute alloys and compounds in the form of bulk and thin films. The studied dilute magnetic semiconductors are $Fe_{0.01}Ge_{1-x}Sb_x$, $Fe_{0.008}Sb_{1-x}Se_x$, $In_{0.95}M_{0.05}Sb$ (M = Mn, Fe, Co and Ni) films and $In_{1-x}Fe_xSb$ (x = 0.00, 0.05, 0.10 and 0.20) bulk systems respectively. The film of $Fe_{0.01}Ge_{1-x}Sb_x$ and $Fe_{0.008}Sb_{1-x}Se_x$ alloys are prepared in two steps. In the first step the bulk sample of respective composition is prepared using Argon arc melting furnace. After the preparation of the bulk alloys, films are prepared on Silicon substrate using thermal evaporation technique. The film of $In_{0.95}M_{0.05}Sb$ (M = Mn, Fe, Co and Ni) is prepared by taking desired quantities of high purity metals and using vacuum sealed in a quartz tube. After vacuum sealing of the bulk materials of $In_{0.95}M_{0.05}Sb$ (M = Mn, Fe, Co and Ni), the samples are heated many times for homogeneity and finally quenched. These quenched samples are used as a source to grow thin films. These $In_{0.95}M_{0.05}Sb$ films are prepared using thermal evaporation technique on Silicon substrate. $In_{1-x}Fe_xSb$ (x = 0.00, 0.05, 0.10 and 0.20) bulk is prepared using the vacuum sealing in a quartz tube. After sealing of $In_{1-x}Fe_xSb$ (x = 0.00, 0.05, 0.10 and 0.20), the samples are heated many times and quenched. The quenched globules are powered structural and hyperfine interaction studies are done.

Different experimental techniques are used for the structural, electrical, surface morphological, magneto-transport and magnetic studies of the respective films. Depending on the materials concerned, some specific properties are measured for some of the materials. The introduction constitutes chapter one while chapter two constitutes the experimental techniques used for various studies and results follow from chapter three to five. The future scope of the present thesis work is also briefed.

Since the choice of suitable host semiconductors is the foremost requirement for the dilute magnetic semiconductors, hence the choice to find out the various properties of different semiconductor materials is the starting point. Once the expected properties of host semiconductors are found, the doping of transition metal is done. By varying the host material concentration in TM doped systems resulted in dilute magnetic semiconducting alloys and compounds.

This chapter consists of brief experimental results and conclusions of dilute Fe doped $Ge_{1-x}Sb_x$ and $Sb_{1-x}Se_x$ thin films, Sb-Se bilayer films, transition metal doped InSb ($In_{0.95}M_{0.05}Sb$, M = Mn, Fe, Co and Ni) films, effects of ion beam irradiation on $Fe_{0.01}Ge_{1-x}Sb_x$ thin films and effects of Iron concentration variation in InSb ($In_{1-x}Fe_xSb$, x = 0.05, 0.10 and 0.20) bulk system.

<u>Chapter 1:</u> Introduction

In chapter one general introduction of dilute magnetic semiconductors and its properties are discussed. The various applications of DMS are also briefly discussed. This chapter includes the ion beam irradiation and how the incident ions interact with the matter is also highlighted. The Motivation of the present thesis is also presented in the chapter one.

<u>Chapter 2:</u> Analytical techniques employed for characterization

Chapter two describes the different techniques of sample preparation and experimental techniques involved in the present work. Some information and basic principle of X- ray diffraction (XRD), Grazing Angle X-ray diffraction (GAXRD), DC resistivity (four probe, two probe and PPMS system), Resistivity versus magnetic field (R-H) using the PPMS system, Scanning electron microscope (SEM), Energy dispersive analysis of X- ray (EDXA), Atomic force microscope (AFM), Magnetic force microscope, Mossbauer spectroscopy, Hall effect measurement, photoluminescence (PL) is discussed.

<u>Chapter 3:</u> Dilute Fe doped $Ge_{1-x}Sb_x$ alloy thin film system

Dilute Fe doped $Ge_{1-x}Sb_x$ (x = 0.01, 0.05 and 0.10) thin films are synthesized using thermal evaporation technique on Silicon substrate. In this chapter the effects of the Sb concentration variation on structural, electrical, surface morphological and magnetic properties of the Fe doped $Ge_{1-x}Sb_x$ thin films are described. These studies are carried out using Grazing Angle X-Ray Diffraction (GAXRD), DC resistivity (four probe technique), Atomic Force Microscopy (AFM) and Magnetic Force Microscopy (MFM) respectively. The X-ray diffraction analysis reveals that the observed pattern is matched with the reflections of Ge (ASTM-JCPDS card No. 65-0334), FeGe (ASTM-JCPDS card No. 20-0516) and $FeGe_2$ (211) (ASTM-JCPDS card no. 89-1982) phases. The crystallite size obtained from the Debye Scherrer formula increases from 29 to 32 nm with an increase in Sb concentration. The Arrhenius plot reveals semiconducting behavior with negative temperature coefficient of resistance. The resistivity results show that activation energy increases with the increase in Sb concentration. The AFM images of alloys show almost uniform particle size distribution with average particle size varying from 35 to 60 nm with an increase in Sb concentration. The MFM images corresponding to the AFM images show the films exhibiting ferromagnetic interactions at RT. The average magnetic domain sizes are observed to increase from 43 to 68 nm with an increase in Sb concentration from x = 0.01 to x = 0.10. With the increase of Sb concentration in $Fe_{0.01}Ge_{1-x}Sb_x$ film resistivity increases for a particular temperature. This change in electrical resistivity indicates that the dopant atoms are contributing to the carrier concentration and mobility. It is depicted from the Arrhenius plot that the activation energy linearly increases with the increases in Sb concentration in a FeGeSb film system. Low temperature transport mechanism (*i.e.* Variable range hopping mechanism) is used to understand the effect of Sb concentration variation at density of states (DOS) in the FeGeSb film system. The surface roughness and particle size is studied using atomic force microscope (AFM). The surface images depicts the increase in particle size and decrease in root mean square roughness due to incorporation of Sb in $Fe_{0.01}Ge_{1-x}Sb_x$ at higher concentration (x = 0.01, 0.05 and 0.10).

This chapter also includes the effects of swift heavy ion beam irradiation on $Fe_{0.01}Ge_{1-x}Sb_x$ thin films. The thin films grown on Si substrate are irradiated with 100 MeV Oxygen (O^{+8}) ions with the fluence rate of 1×10^{12} ions/cm^2. The effect of irradiation on structural, electrical and morphology of films is discussed.

<u>Chapter 4:</u> Dilute Fe doped $Sb_{1-x}Se_x$ and SbSe bi-layer thin film system

The outcomes of different studies of $Fe_{0.008}Sb_{1-x}Se_x$ alloy thin films having different concentrations of Se grown on Si substrate and bilayer Sb-Se films with varying thickness of Se layer is elaborated in this chapter respectively. The $Fe_{0.008}Sb_{1-x}Se_x$ films reveal metal to semiconductor phase transition above RT of all the films. This transition property of Fe doped $Sb_{1-x}Se_x$, can be used in temperature sensor applications. The density of states is Se concentration dependent in the system and it decreases with increase in Se concentration. Surface topography of the film reveals that there is an increase in particle size and average roughness with an increase in Se concentration. The results of MFM images for different Se concentration reveals that the magnetic effect is due to charge carriers induced polarization of Fe local moments and the absence of magnetic clusters. The observed magnetic domain size is Se dependent and varies from ~ 54-69 nm for x = 0.01-0.10.

The results from XRD and AFM for the Sb-Se bilayer film shows that crystallite size after irradiation (Ag^{+15} ions, 200 MeV energy) increases while the particle size decreases. From the AFM images it seems, the observed particles are not single crystals but are made-up of few crystallites. It is observed that due to irradiation the particle size decreases than as deposited, but the crystallinity of the film improves much more than that of as deposited film.

Chapter 5: Studies of Iron doped InSb bulk and TM doped InSb films

The outcomes of different Iron concentration doped InSb bulk and different TM-doped InSb films grown on Silicon substrate are elaborated in this chapter. The $In_{1-x}Fe_xSb$ bulk is studied for x = 0.00, 0.05, 0.10 and 0.20 respectively. In the $In_{1-x}Fe_xSb$ (x = 0.00, 0.05, 0.10 and 0.20) bulk system the XRD peaks are indexed based on cubic structure (JCPDS file no. 89-4299) of InSb with $F\bar{4}3m$ space group. With the inclusion of Fe in higher concentration at Indium site another phase of InSb appears (JCPDS card no. 47-1502). With the increase in amount of Iron in InSb bulk, the shift in the XRD peak towards lower 2θ value is observed that depicts the inter-planer spacing enhancement with the increase in Fe concentration. The crystallite size of the $In_{1-x}Fe_xSb$ increases with the increase in Fe concentration. From the Mossbauer spectra of $In_{1-x}Fe_xSb$ bulk system two different sites A (quadrupole site) and B (singlet site) is observed. For the site A with a lower concentration of Iron (x = 0.05) isomer shift is maximum and it is found to be 0.69±0.02 mm/sec and with the increase in Iron concentration the isomer shift of this site (site A) decreases from 0.69±0.02 to 0.42±0.02 mm/sec (for x = 0.20). While the isomer shift for site B approximately constant for x = 0.05 to 0.20. The quadrupole splitting (site A) for x = 0.05 is maximum and the obtained value is 0.89±0.02 mm/sec but with the increase in Iron concentration the quadrupole splitting decreases from 0.89±0.02 to 0.36±0.02 for x = 0.20 in $In_{1-x}Fe_xSb$ bulk system. The population for site A increase with the increase in Iron concentration while for site B it decreases with the increase in Iron concentration. The site B (singlet site) is attributed to the cubic phase. The site A is attributed to another phase of InSb which is non-cubic and hence quadrupole splitting is observed. The value of the quadrupole splitting decreases with the increase in Iron concentration in InSb which depicts that the site A is going towards symmetry.

The four different transition metals *i. e.* Mn, Fe, Co and Ni are doped in InSb to make thin films with composition $In_{0.95}M_{0.05}Sb$ (M = Mn, Fe, Co and Ni). Their structural, electrical, surface morphological, magneto-transport and magnetic studies is presented. The un-doped and TM doped InSb film has f.c.c. structure with $F\bar{4}3m$ space group. The structure of un-doped InSb film matches with the JCPDS card no. of 73-1985. In the XRD diffraction pattern no peak/peaks of transition metal dopants like Fe, Co, Mn and Ni or its phases are seen. The un-doped and TM doped InSb film shows semiconducting nature, having a negative temperature coefficient of resistance. With the incorporation of transition metal (Mn, Co and Ni) in InSb films resistivity increases while in case of Fe doping resistivity decrease as compare to un-doped InSb film. The activation energy also increases on inclusion of Mn, Co and Ni in InSb film while it decreases on Fe doping. In order to explain the conductivity mechanism in TM doped InSb films variable range hopping theory is used which fits well for both the lower as well as a high temperature range of 100-150 and 210-350 K. This theory suggests that the density of states at the Fermi level decreases due to inclusion of Mn, Co and Ni while it increases with Fe doping. The magnetotransport properties of transition metal doped InSb are also studied using the PPMS system at different temperature. The magnetotransport measurement is done upto applied field of 5 tesla. The un-doped InSb film shows the 2.4 % variation in magnetoresistance at 20 K. This change in resistance saturates beyond 1.5 T field. When Mn is doped in InSb film the observed magnetoresistance is 4.7 % at 20 K. Above this temperature (20 K $<$ T $<$ 300 K) in $In_{0.95}Mn_{0.05}Sb$ film no significant change in magnetoresistance is observed. At 20 K the MR value increases with the applied field and saturates when the applied field is increased beyond 1.5 tesla. At 300 K temperature a negative magnetoresistance ratio is observed with the value of -3.2 %. The $In_{0.95}Ni_{0.05}Sb$ film shows the MR variation of 4.0 % at 20 K temperature. The MR variation ratio in the Ni doped InSb film is observed to be saturated with the increase in applied magnetic field after 2.5 tesla at 20 K. The temperature between $20 < T < 300$ K, there is no significant change in MR ratio with the increase in magnetic field. At RT (~ 300 K) 2.3 % MR ratio variation is observed in the 5 tesla field. It is observed that MR ratio variation in $In_{0.95}Fe_{0.05}Sb$ at 5 K temperature is maximum and it is observed to be ~ 0.055 %. The observed MR ratio variation decreases with the increase in temperature from 5 K to 200 K. The AFM images of un-doped and doped with transition metal shows that particles are distributed evenly on the surface of the films. The AFM studies reveal that the root means squared (rms) roughness decreases with doping of TM as compare to un-doped film. The rms roughness for TM doped films is in the range of 2- 13 nm while for un-doped film it is 18.27 nm. The average peak height and maximum peak height of TM doped films also decreases as compare to un-doped InSb film. For the TM doped films the average peak height and maximum peak height are in the range of ~ 5- 35 and ~ 7- 66 nm respectively. While the average peak height and maximum peak height for un-doped film is ~ 50 nm and ~ 82 nm respectively. The MFM image shows that there is no magnetic interaction in un-doped film. It is observed that in $In_{0.95}Mn_{0.05}Sb$ film magnetic contrast is visible and the magnetic domains are uniformly distributed. The MFM images of Fe, Co and Ni doped InSb films depict the weak magnetic interaction at the surface of the film. It also shows the absence of Co, Fe and Ni clusters or Co, Fe and Ni related any phase with InSb film respectively. In the magnetization versus temperature studies of $In_{0.95}Fe_{0.05}Sb$ film, the ZFC magnetization curve increases as low temperature, reaching a maximum at temperature ~ 65 K with magnetic moment value of 4.602×10^{-6} emu. The

ZFC curve shows the antiferromagnetic to paramagnetic transition at ~ 25 K. The magnetic moment does not drop to zero, suggesting a high Curie temperature beyond RT. The DC magnetization (ZFC and FC) ZFC and FC curves for Mn doped InSb decreases with the decrease in temperature from 300 to 50 K, which is consistent with the conventional antiferromagnetic nature of $In_{0.95}Mn_{0.05}Sb$ film. The ZFC curve for Mn doped InSb film shows the contribution of the super paramagnetic particles to the resultant moment. The ZFC results indicate that at ~25 K there is a spin fluctuation at low temperature and spin reorientation takes place in $In_{0.95}Mn_{0.05}Sb$ film. The same kind of phenomenon also occurs in the $In_{0.95}Co_{0.05}Sb$ film. The only difference is in Co doped system is there seems to be less strain as compared to the Mn doped system. This splitting of the ZFC and FC curves in $In_{0.95}M_{0.05}Sb$ (M = Fe, Mn and Co) may be appearing due to the co-existent system of antiferromagnetic and ferromagnetic phases. This splitting of ZFC and FC magnetization at low temperature also reveals spin glass transition in $In_{0.95}M_{0.05}Sb$ (M = Fe, Mn and Co) films grown on Silicon substrate.

The magnetic moment versus applied magnetic field (H) curve (M-H curve) of $In_{0.95}Fe_{0.05}Sb$ film at 10 K temperature. The figure shows the hysteresis behavior of $In_{0.95}Fe_{0.05}Sb$ film. The value of coercivity and the residual magnetization is found to be ~ 100 Oe and 6.8811 emu respectively from the hysteresis curve of $In_{0.95}Fe_{0.05}Sb$ film.

The work to be carried out in future

After investigating the structural, electrical, surface morphology and magnetic properties of dilute transition metal doped $Fe_{0.01}Ge_{1-x}Sb_x$ (x = 0.01, 0.05 and 0.10), $Fe_{0.008}Sb_{1-x}Se_x$ (x = 0.01, 0.05 and 0.10), $In_{0.95}M_{0.05}Sb$ (M = Fe, Co, Mn and Ni) films and $In_{1-x}Fe_xSb$ bulk; further work is to find new dilute transition metal doped semiconductors and investigate their characteristics. Hence it is proposed that

1. To extend the similar kind of study to search new DMS alloys and compounds in the form of bulk and thin films within the solubility limit, so that these can be used for practical spintronics applications. In Ge based system the behavior of another 3-d metals like Co, Mn, Ni etc. can give rise to many interesting facts. Hence it will also be interesting to see the effect of these transition metal doping on Ge-Sb system.
2. The rare earth materials due to their partially filled f- orbitals are also a good candidate for DMS materials. Therefore, research in these rare earth materials may lead to novel materials suitable for technological applications.
3. A part of this thesis work focused on transition metal doped InSb films (*i.e.* $In_{0.95}M_{0.05}Sb$, M = Fe, Mn, Co and Ni). In order to understand the origin of spin glass behavior as observed in DC magnetization of the $In_{0.95}Fe_{0.05}Sb$, $In_{0.95}Mn_{0.05}Sb$ and in $In_{0.95}Co_{0.05}Sb$ films AC magnetization will be performed. AC susceptibility will be measured by varying the frequency. In a spin glass system, a magnetic spin experiences random interaction with other magnetic spins, resulting in a state that is highly irreversible and metastable. The AC susceptibility measurement is particularly important for spin glasses because it determines the freezing temperature accurately.