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Disordered Electronic and Magnetic Systems - Transition Metal (Mn) and Rare Earth (Gd) Doped Amorphous Group IV Semiconductors (C, Si, Ge)

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Materials Science and Engineering

by

Li Zeng

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2007
The dissertation of Li Zeng is approved, and it is acceptable in quality and form for publication on microfilm:

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2007
To dear Mom and Dad,
always
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   Thin Film Deposition
   Experimental Solid State Physics
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ABSTRACT OF THE DISSERTATION

Disordered Electronic and Magnetic Systems - Transition Metal (Mn) and Rare Earth (Gd) Doped Amorphous Group IV Semiconductors (C, Si, Ge)

by

Li Zeng

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2007

Professor Frances Hellman, Co-Chair
Professor Sungho Jin, Co-Chair

While the physics of electrical doping of semiconductors has been well understood for decades, magnetic doping and the interactions between the carriers and the magnetic moments in semiconductors are still under active investigation for various applications, such as spintronics and quantum computing. Our systematic studies on transition-metal-doped (TM-doped) and rare-earth-doped (RE-doped) amorphous group IV elemental semiconductors provide unique insight into the rich physics of this type of materials.

Our model system is the e-beam coevaporated $a$-Gd$_x$Si$_{1-x}$ films. Magnetron cosputtered $a$-Gd$_x$Si$_{1-x}$ films, despite having very different film morphology at the 10-nm scale from the e-beam coevaporated films, are demonstrated to possess almost the same physical properties. Cosputtered $a$-Gd$_x$C$_{1-x}$(:H$_y$) and Gd ion-implanted $ta$-$C$ ($ta$-$C_{1-x}$:Gd$_x$) films are studied for Gd in different $a$-$C$ matrices with different $sp^2/sp^3$ ratio. All doped $a$-$C$ films are on the insulating side of the metal-insulator transition. Very similar to $a$-Gd$_x$Si$_{1-x}$ films, Gd possesses a large magnetic moment in $a$-$C$. The moment-moment and moment-carrier interactions lead to a spin-glass ground state and large negative magnetoresistance (MR) below a crossover temperature $T'$ in both $a$-Gd$_x$C$_{1-x}$(:H$_y$) and $ta$-$C_{1-x}$:Gd$_x$ films. A small positive MR is found above $T'$. 
Transition metal Mn has always been believed to possess a large local moment in Si or Ge. However, e-beam coevaporated $a$-Mn$_x$Si$_{1-x}$ films are found to show a quenched local moment for Mn concentration as low as $x=0.005$ and up to $x=0.175$. All films are purely paramagnetic and have very small saturation moments. Unlike Gd, which provides both carriers and local moment, Mn only provides electrical carriers in $a$-Si. These results suggest an itinerant non-magnetic Mn states in $a$-Si; the insulating behavior is a result of the strong structural disorder. This quenching of the local Mn moment has not been predicted by any existing theory. Consistent with the small Mn moment, $a$-Mn$_x$Si$_{1-x}$ films show a very small positive MR, in contrast to Gd-doped films.
1

Introduction

1.1 Magnetic Semiconductors

Magnetic semiconductors have become a hot research topic in recent years because of the vision to utilize the electron spin in electronics. The so-called spintronics [1] is a relatively unexplored field compared to modern electronics based on semiconductor materials. The basic idea of spintronics is to utilize electron spin in addition to electron charge, thus one more degree of freedom of the electron properties can be used for information storage, communication and logic computing. The early spintronics examples are all-metal-based multilayer structures, such as the well-known ferromagnet/nonmagnetic/ferromagnet multilayer sandwich structure which has giant magnetoresistance (GMR) effects [2]. The GMR materials soon found their applications in magnetic hard-disk read heads, which greatly assisted the scaling-up of hard-disk capacities. The six-year transformation from fundamental scientific discovery to real-life application is one of the greatest living examples of how basic science can help to advance modern technology. This success has stimulated more scientific research in this direction. As the author is writing this dissertation, both founders of the GMR materials, Dr. Albert Fert and Dr. Peter Grünberg, share the Nobel prize in Physics 2007 “for the discovery of Giant Magnetoresistance”.

The art of manipulating electron charge in semiconductor materials has been developed for many decades. Semiconductors are solid state materials with a
finite energy band gap and can be effectively doped either with electrons (n-type) or holes (p-type). Their electrical properties (conductance) can be tuned many orders of magnitudes by the doped extra electron states in the band gap near the band edges. Through band engineering, such as the formation of p-n junctions and metal-oxide-semiconductor (MOS) structures, tuning the charge flow channel can be realized by an applied electrical field. However, in all modern semiconductor applications, the spin of the electron is ignored. Since all popular semiconductor materials are nonmagnetic, charge carriers have random spin orientations, unlike in ferromagnetic (FM) metals which have unbalanced density of states (DOS) at the Fermi level for spin-up and spin-down electrons, respectively. Thus in FM metals, charge currents are also spin polarized (spin-polarized current).

As we have discussed so far, early spintronics are based on FM materials, which are metals like Fe, Ni Co, Gd or their alloys, while electronics are based on technologically important semiconductor materials, such as group IV elemental semiconductors, group III-V and group II-IV compound semiconductors etc, which are nonmagnetic in nature (means not FM). We know how to control one property of the electron, either the charge or the spin, in the corresponding material. A new game plan for spin electronics is to control both properties at the same time in a new hybrid way. To achieve such an ambitious goal, a novel material is needed, which should in principle, have both the merits of a semiconductor and of a ferromagnet. This new type of material is naturally named as magnetic semiconductor.

The research on magnetic semiconductors has a long history and involves a large class of materials. Classic examples are europium chalcogenides [3], Gd$_{3-x}$xS$_4$ [4] and dilute magnetic systems, such as (Cd$_{1-x}$Mnx)Te with Mn randomly distributed throughout the cadmium sublattice [5]. The common feature of these seemingly quite different material systems is that they are all semiconductors containing magnetic ion cores with significant moment-carrier interactions which lead to moment-moment interactions and magnetic orderings. This gives interesting properties to these materials such as a carrier-induced ferromagnetism [6] or a magnetic field-tuned insulator-metal transition [4].

An important leap in this field is marked as the discovery of ferromagnetism
with relatively high Curie temperature \( T_C \) in Mn-doped InAs and GaAs [7], which are technologically important III-V compound semiconductors. By using modern non-equilibrium thin film growth methods, metastable phases of (In, Mn)As and (Ga, Mn)As thin films can be prepared. For example, by doping 3.5% Mn (the magnetic center) in GaAs using low-temperature molecular beam epitaxial (MBE) growth, the resulting (Ga,Mn)As is FM with a \( T_C \) of 60 K [8].

Unlike the classic magnetic semiconductor europium chalcogenides, where the magnetic ion has the stoichiometric composition as part of the semiconductor matrix, Mn is introduced as a magnetic dopant in III-V compound semiconductors with a diluted concentration, similar to the earlier example of Mn-doped II-V system: (Cd, Mn)Te. Thus the latter two systems belong to the same class of material, named as diluted magnetic semiconductor (DMS). Following Ohno’s route, many promising DMS systems have been explored. One of the most studied examples is the III-V model system: Mn-doped GaAs with Mn substituting for Ga [(Ga, Mn)As]. \( T_C \sim 150 \text{ K} \) has been achieved and the ferromagnetism is believed to be hole-mediated [9]. Although the \( T_C \) is still below room temperature, (Ga, Mn)As has been used as a test bed for simple spintronic devices. (In, Mn)As and (Ga, Mn)P have also been studied but with lower \( T_C \). The most promising III-V candidate for room-temperature magnetic semiconductor is (Ga, Mn)N. However, the nature of the experimental determined ferromagnetism is still controversial [10].

In II-VI compound semiconductors, there exists at least three groups of behavior. First, the existence of structurally coherent but chemically inhomogeneous nanocrystalline phases may account for the observed ferromagnetism. For example, above room-temperature ferromagnetism in (Zn, Cr)Te is suggested to be related to a metallic CrTe or Cr-rich (Zn, Cr)Te phase with a magnetic ordering temperature \( \sim 320 \text{ K} \) [10]. One argument is that since the double-exchange interactions between Cr ions is short-range, a large local Cr concentration is needed for FM ordering. However, there is also experimental evidence based on magnetic circular dichroism (MCD) that indicates a homogeneous phase with intrinsic coupling between local moments and carriers [11]. The second group includes heavily doped \( p-(Zn, Mn)Te \). Like (Ga, Mn)As and related semiconductors, a hole-mediated ferromagnetism can describe their physical properties. Finally, in oxide semicon-
ductors, both ferromagnetism and semiconducting behaviors have been observed. However, clustering of metal oxides [such as Mn oxides and Co oxides, which are FM or antiferromagnetic (AFM) with high $T_C$ or Néel temperature ($T_N$)] is hard to exclude. Note that even AFM nanocrystallites, with a very high $T_N$, can give significant magnetic signals due to large uncompensated surface spins below a blocking temperature.

In the III-V and II-VI compound semiconductors, mean-field theory based on $p$-$d$ Zener model suggests that higher $T_C$ is achievable in wide band gap materials, such as in Mn-doped GaN or Co-doped ZnO [12]. Above room temperature FM was indeed first observed experimentally in these two semiconductors, though whether the origin is intrinsic or not is still under debate. In group-IV elemental semiconductors, however, DMS was first claimed in Mn-doped Ge with a narrow band gap [13]. And according to the first-principles calculation, Mn-doped Ge is half-metallic due to lower degree of hybridization compared with Mn-doped Si, which just misses the half-metallicity [14]. So far, there have been only two groups claiming FM behavior of Mn$_x$Si$_{1-x}$ for even above room temperature, but the results and explanations are very controversial [15–17]. Recent sub-micron scanning photoelectron microscopy (SPEM) study, which is capable of mapping the chemical distribution, have also shown chemical inhomogeneity in Mn-doped crystalline Ge (c-Ge$_{1-x}$Mn$_x$) [18]. High-resolution transmission electron microscopy (HR-TEM) and synchrotron x-ray diffraction have detected the existence of MnSi$_{1.7}$ (including a family of Mn silicides: Mn$_4$Si$_7$, Mn$_{11}$Si$_{19}$, Mn$_{15}$Si$_{26}$ and Mn$_{27}$Si$_{47}$) nano-crystallites in c-Si$_{1-x}$:Mn$_x$ [19]. The ferromagnetism in these systems is likely to originate from the Mn-rich Ge phase [18] and MnSi$_{1.7}$ nano-crystallites [19], respectively.

The list of potential DMS systems studied in the literature is a long one and is still rapidly growing. It is not the author’s intention to give a comprehensive summary, but instead, a brief introduction to this interesting topic as one of the motivations for this dissertation. Interested readers are encouraged to refer to the recent review articles in Refs. 5,10,11,20.
1.2 Amorphous Semiconductors

A perfectly ordered crystalline material is the exception rather than the rule in reality. Disorder exists in a great variety of degrees, ranging from a random distribution of a few impurity centers in an otherwise perfect crystal, to strongly disordered material systems, such as multi-component alloys and amorphous materials. The structure of amorphous materials with no long-range order is not as well defined as the crystalline counterpart, thus it is hard to model their physical properties. Nevertheless, these difficulties have not prevented people from discovering their technological importance for many applications. For semiconductor materials in the amorphous form, amorphous Si (a-Si) is a great example for its application for flat panel displays and solar cells. There are two main driving forces to use a-Si: the low manufacturing cost compared with single-crystalline Si; and the easiness to passivate dangling bonds compared with poly-crystalline Si.

The microstructure of a-Si is a continuous random network (CRN) of tetrahedrally-bonded Si atoms [21], in contrast to dense random packing of hard spheres (DRPHS) model for metal alloys [22]. The Si-Si bond angles and bond lengths vary somewhat from the equilibrium values found in single crystalline Si (c-Si) due to disorder. Major defects are Si dangling bonds, which can be passivated by doping often with H. In research labs, high quality a-Si can be achieved by low-temperature $e$-beam evaporation with $>98\%$ mass density of the c-Si [23]. An increase of absorption coefficient near $\sim 1.1$ eV indicates that a-Si possess an optical band gap with similar value to that found in c-Si, but it is no longer an indirect band gap due to the relaxation of the $k$-selection rule [21]. There are also strongly localized states forming a band tail due to the structural disorder and deep-level mid-gap states due to the Si dangling bonds in a-Si.

One advantage of a-Si thin films is their flexibility to incorporate foreign atoms, such as large ions like Gd. The Si-Si covalent bonds near the dopants can be deformed to accommodate the large local stress very effectively within a short distance and have been shown to fully relax to their ordinary tetrahedral configuration one atom away from the doped ion [24]. The result is that up to 20% doping, the atomic number density of $a$-Gd$_x$Si$_{1-x}$ is still very close to that of the
undoped $a$-Si, and independent of Gd $x$ [25]. Along with the low temperature thin film growth process, large concentration of dopant atoms can be “frozen” in the $a$-Si matrix to form a homogeneous doped phase [26].

Amorphous carbon ($a$-C) is another widely studied amorphous group IV material. It is mainly used for its good mechanical properties and chemical inertness, such as the protective coating for magnetic hard disks or the mask for chemical etching in thin film process. What is less known is that $a$-C can also be a semiconductor. The $sp^3$-bonded crystalline carbon phase is diamond, a well-known wide band gap semiconductor. However, unlike $c$-Si and $c$-Ge, the thermodynamic stable phase is not the $sp^3$-bonded diamond structure, but the $sp^2$-bonded graphite instead. With a hexagonal layered structure, graphite is a semi-metal with conducting basal plane. A typical $a$-C film will have a mixture of $sp^2$ and $sp^3$ bonding schemes, and its properties strongly depend on the $sp^2/sp^3$ fraction. $a$-C with high $sp^3$ fraction is often called the tetrahedral amorphous carbon ($ta$-C). $ta$-C has very high mechanical hardness and electrical resistivity, like the diamond. High energy deposition, such as ion-beam deposition which accelerates the deposited ions using an applied voltage, is needed to stabilize the metastable $ta$-C phase. To be a useful semiconductor material for electronic application, both $n$- and $p$-type dopings are needed. While B is demonstrated to be an effective $p$-type dopant for $ta$-C, a good $n$-type $ta$-C for example using N as the dopant has not been so successful.

Doped amorphous semiconductors, such as $a$-Si and $a$-Ge, have a metal-insulator ($M$-$I$) transition similar to their crystalline counterparts, such as Si:P. Due to the Anderson localization, the critical doping where the $M$-$I$ transition occurs is $\sim$0.1, orders of magnitude higher than in doped crystalline semiconductors. In this dilute concentration range, metal dopants, such as Cr, Fe or Co, do not possess a local moment in $a$-Si or $a$-Ge [27–30]. For instance, in amorphous Fe$_x$Me$_{1-x}$ ($Me = Si, Ge, Sn$), there is a threshold concentration, $\sim$0.4, for the onset of magnetic ordering which may result from interactions between localized giant moments that exist only above this concentration [30, 31]. Below $x=0.4$, the Fe moment is less than 0.1 $\mu_B$. This may explain why no large effect of magnetic moment is found near the $M$-$I$ transition critical concentration $\sim$0.1 [28], quite different from the rare-earth Gd-doped $a$-Si or $a$-Ge where Gd moments have large effects near the
M-I transition due to the more localized $f$ electron shell $[32, 33]$. Mn is another popular transition metal dopants as mentioned in DMS studies. For Mn-doped $a$-Si, films near the $M$-$I$ transition were reported to have very small positive magnetoresistance $[34]$. There is no magnetization study for $a$-Mn$_x$Si$_{1-x}$ near the $M$-$I$ transition in the literature and our work on e-beam coevaporated $a$-Mn$_x$Si$_{1-x}$ in Chapter 6 fills the vacancy. It is found that Mn does not possess a local moment in $a$-Si, in contrary to existing models and calculations $[14, 35]$. Chapter 7 will present some preliminary results which show, however, local Mn moments do appear in $a$-Ge. These amorphous semiconductors doped with various transition or rare-earth metals provide a rich field for studies for the 3D $M$-$I$ transition and interactions between moments and charge carriers by measuring their transport, magnetization and magnetotransport properties.

1.3 Magnetoresistance (MR)

Magnetoresistance (MR) measures the change of electrical resistance ($R$) with applied field ($H$). MR effects are ubiquitous in almost all types of materials, although the sign, the amplitude, the temperature and field response of MR are quite different based on quite different underlying physics. In this section, a brief survey of different types of MR in single phase (undoped or doped) material systems will be presented. MR of artificial material structures, such as GMR and tunneling MR (TMR) in multilayer systems will not be discussed here. Also, all discussion is restricted to the 3D limit unless otherwise stated. Equations and examples are given based on electrons, but can be equally applied for holes with the opposite charge.

In this dissertation, MR is defined as:

$$MR = \frac{\Delta R}{R_H} = \frac{\rho(H,T) - \rho(H=0,T)}{\rho(H,T)}$$  

(1.1)

where $\rho(H=0,T)$ is the zero field resistivity and $\rho(H,T)$ is the resistivity in a magnetic field. The change of resistance ($\Delta R$) is normalized by $R_H$ in order to be consistent with the magnetoconductance (MG) usually defined in theoretical
papers:
\[ MG = \frac{\Delta G}{G_0} = \frac{\sigma(H,T) - \sigma(H = 0,T)}{\sigma(H = 0,T)}. \]  \tag{1.2}

Since \( \rho = 1/\sigma \), one can derive mathematically that \( MG = -MR \).

### 1.3.1 Lorentz MR (LMR) in Nonmagnetic Metals

For a moving electron in a magnetic field, a magnetic force \( \vec{F}_L \) is exerted on the electron with the force direction always perpendicular to the direction of its velocity \( \vec{v} \) according to the Lorentz law:
\[ \vec{F}_L = e\vec{v} \times \vec{B} \]  \tag{1.3}

In a simple free electron model, the Lorentz force will be exactly balanced by the electrical force of the Hall field developed in the \( \vec{j} \times \vec{B} \) direction across the two sample boundaries [36]. Thus once steady state is achieved, there is no modification of the electron average velocity (drift velocity \( \upsilon_d \)) along the \( \vec{j} \) direction and no changes in the sample conductivity with field:
\[ \sigma = \frac{ne^2\tau}{m}. \]  \tag{1.4}

where \( n \) is the electron density, \( m \) is the free electron mass and we have assumed a single relaxation time (\( \tau \)) which does not depend on the electron velocity. However, individual electrons near the Fermi surface have Fermi velocity \( \upsilon_F \) which is quite different from the \( \upsilon_d \). Therefore an electron at the Fermi surface still experiences a non-zero \( \vec{F}_L \) thus in general moves in a cyclotron orbit and scatters more. This effectively reduces \( \tau \) thus decreases \( \sigma \). This simplified picture is adequate to explain the sign of the LMR, which is always positive (resistance increases after applied a magnetic field).

In the nearly free electron model for metals and semiconductors, an electron moves as a Bloch wave packet in the conduction band of the host crystal. Eq. 1.4 still holds, but one needs to replace the free electron mass \( m \) by the effective mass \( m^* \). The Lorentz force keeps an electron moving on a constant energy surface, with its orbital plane in \( k \) space normal to the direction of \( \vec{B} \). For LMR effects, only the electrons on the Fermi surface, which is the surface of constant energy \( \epsilon_F \).
in \( k \) space, are important since scattering events only occur at the Fermi surface where empty energy states are available. In the crystal, the free electron Fermi surface is modified by the periodic lattice and leads to quite different orbits, such as electronlike orbits, holelike orbits and open orbits. LMR is now very sensitive to the shape and connectivity of special types of orbits known as the extremal orbits, as well as their directions with respect to the \( \vec{B} \) field. In practice, LMR effects have been used as a powerful experiment method for the determination of Fermi surfaces of metals. An example is the Shubnikov-De Haas (S-dH) oscillation in the field dependence of the MR [37].

Under ordinary conditions where the magnetic field is not so strong to break down the band structure, the LMR usually has a quadratic field dependence. The most important quantity to estimate the MR is \( \omega_c \tau \) [37], where \( \omega_c \) is the electron cyclotron frequency:

\[
\omega_c = \frac{eH}{m^*c}
\]  

(1.5)

and \( \tau \) is related to the sample \( \sigma \) (Eq. 1.4) and the carrier mean free path \( l \):

\[
l = v_F \tau
\]  

(1.6)

Therefore, a useful expression of \( \omega_c \tau \) related to experimental variables is:

\[
\omega_c \tau = \frac{H \sigma}{nec}
\]  

(1.7)

The physical meaning of \( \omega_c \tau \) can be viewed as the average rotation angle around the cyclotron orbit between scattering events. \( \omega_c \tau \) should be as least of order 1 to have substantial MR. From Eq. 1.7, one can see that LMR strongly depends on the sample conductivity \( \sigma \) (thus \( l \) and \( m^* \)) and the carrier density \( n \).

The ubiquity of the Lorentz force of the magnetic field on a moving charge and the consequent decrease in \( l \) with \( H \) suggests that positive MR should be observed dominantly in nature. However, LMR is usually a small effect in ordinary metals such as Cu and Au under normal conditions (polycrystalline samples at small field, room temperature). In Cu, for example, \( \omega_c \tau \ll 1 \) at room temperature due to the large carrier density \( n \), short mean free path and large effective mass. So MR for Cu is negligible, and increases to a few percent only when \( \sigma \) becomes large at low temperature for really clean samples. The LMR, in general, can be easily
masked by other larger MR effects (originating from interactions experienced by the electron), such as spin-orbit, electron-phonon, exchange and coulomb interactions etc, where the nearly free electron model is no longer valid.

One extraordinary exception is bismuth [38,39], a nonmagnetic metal with quite large LMR when the crystal quality is good in the thin film form. The reported MR (400000% at 5 K and 330% at 300 K [37, 40]) is even larger than the GMR effect. This is because Bi is a semimetal with unusual transport properties. It has a highly anisotropic Fermi surface (with both electron and hole pockets), low carrier densities (a semimetal), small carrier effective masses and a long carrier mean free path [40]. \( \omega_c \tau \) of Bi is much larger than that of Cu based on Eq. 1.7 (although the nearly free electron model is no longer valid for Bi). Such large LMR effect has been known for a while [38], and was found to be very sensitive to the sample quality. This phenomenon was rediscovered in high quality single crystal thin films prepared by electrodeposition which gives very high MR values even at room temperature [37].

### 1.3.2 Anisotropic MR (AMR) in FM Metals

AMR (also known as the extraordinary MR) in FM 3d transition metal alloys was reviewed by McGuire [41]. The effect is anisotropic because the sample resistivity depends on the relative orientation between the electrical current \( I \) and the applied field \( H \). Contrary to LMR [also known as the ordinary MR (OMR)], for some 3d alloys, the longitudinal resistivity (\( \rho_\parallel \), measured with the current parallel to the field) is higher than the transverse resistivity (\( \rho_\perp \), measured with current perpendicular to the field). Therefore, the Lorentz force cannot explain the origin of AMR. AMR is usually found to be negative at small fields near \( T_C \), which is especially interesting. The origin of AMR is due to spin-orbit (SO) coupling and \( d \)-band splitting, as well as their effects on \( s-d \) scattering. SO interactions modify the Fermi surface by lowering its symmetry, therefore leads to anisotropic scattering which gives rise to the difference between \( \rho_\parallel \) and \( \rho_\perp \). The \( d \)-band splitting upon FM ordering decreases the majority spin states of the \( d \) band at the Fermi surface \( [N_d(\epsilon_F)] \), so the \( s \) electron relaxation time (\( \tau_s \)) increases since \( \tau_s \) is known
to be inversely proportional to $N_d(\epsilon_F)$. Therefore the resistivity drops with the spontaneous magnetic ordering in 3$d$ transition metals where $s$-$d$ scattering is the dominant feature, explaining the negative MR near $T_C$.

At room temperature, the AMR effect for Ni-Fe or Ni-Co alloys can be as high as 5% thus has important technological application. This effect was used for the read head in magnetic recording devices for many decades until GMR materials were introduced.

### 1.3.3 Colossal MR (CMR) in Oxides

The phrase CMR was first coined by Jin et al. in order to distinguish the much larger MR effect found in the perovskite structure manganite La-Ca-Mn-O from the GMR effect [42]. About -1500% MR in a 60 kOe field was found near the antiferromagnetic to ferromagnetic (AFM-FM) transition in this material. The AFM-FM transition is also accompanied by an insulator to metal ($I$-$M$) transition; the CMR is explained by the field-induced magnetic ordering near $T_C$. The simultaneous occurrence of ferromagnetism and metallicity in these oxides can be explained by the double-exchange mechanism developed by Zener [43]. According to Zener’s double exchange model, the electron hopping is favored if the neighboring Mn sites are ferromagnetically aligned. Therefore, above the transition temperature in the AFM phase, electron hopping is hindered thus the sample is insulating (with an activated hopping conductivity). As the temperature decreases, the system lowers the total energy by undergoing a FM ordering, which greatly enhances the electron kinetic energy and forms an itinerant band. However, double exchange alone can not explain the large magnitude of the CMR near the transition. Electron-phonon coupling associated with Jahn-Teller (J-T) distortion is also suggested to play an important role [44].

Due to the large MR effect, CMR materials are regarded as promising for applications (the large fields required is the biggest obstacle) as well as an important playground for fundamental studies of strongly correlated systems where electron-electron interactions are important. CMR materials also often are entirely spin polarized at $\epsilon_F$, leading to large magnetic tunneling junction (MTJ) effects. Oxide
compounds with similar CMR effects were later found in pyrochlore and spinel-based materials. The origin of CMR is still a rich field to explore [44].

1.3.4 MR in Semiconductors

In In-Sb semiconductor with high electron mobility, a positive MR is found in the high-field, low-temperature limit due to field-induced shrinkage of the electron orbital at the impurity sites [45]. This reduces the overlap of the wave function of adjacent donors and has the largest effect on transport properties near the $M$-$I$ transition. This can be viewed as an analog to the classic Langevin diamagnetic response of current loops to $H$, where the induced change of moment always opposes the change of $H$. At 100 mK, MR~38% at 1100 Oe and does not saturate. In the same material, MR is negative in the low-field limit due to the localization effect, which is the consequence of the disorder. The localization effect could be a dominant effect in strongly disordered amorphous materials.

In disordered electronic systems, due to quantum interference of self-intersecting paths in the presence of time-reversal symmetry (no magnetic field), electrons tend to be localized in a length scale called $L_{Th}$. Applying a magnetic field will break the time-reversal symmetry thus reduce $L_{Th}$. This is the weak localization effect which accounts for the small negative MR in non-magnetic disordered electron systems, such as $a$-Nb$_x$Si$_{1-x}$ and $a$-Au$_{1-x}$Ge$_x$ [46].

In the magnetic semiconductor Gd$_{3-x}$S$_4$ ($\nu$: Gd vacancy), a large negative MR was found [4]. The $x=0$ end member is Gd$_3$S$_4$, a FM metal, and the $x=1/3$ end member, Gd$_2$S$_3$ is an AFM insulator. There are two possible localization effects in this system. One is the potential fluctuation due to the random distribution of the Gd vacancies. The other is due to the exchange interaction of conduction electrons with magnetic Gd$^{3+}$ ions. In the latter case, a bound magnetic polaron (BMP) is formed. In the insulating phase, a large FM paloron in an AFM background has a short localization length and large hopping energy. Applying an $H$ field will align the moments and therefore, reduce the sample resistivity. A $H$-tuned $M$-$I$ transition was observed in this material. The BMP model can explain negative MR in many materials systems in a similar fashion, such as for the DMS (Cd,
Mn)Te and (Ga, Mn)As.

1.3.5 MR in Magnetically Doped Amorphous Semiconductors

A new class of materials, the magnetically doped amorphous group-IV semiconductors, are the focus of this dissertation. These materials show enormous negative MR below a characteristic temperature. The fundamental origin of this large MR in semiconductor has not been fully understood and no existing theories explains all the aspects of this rather dramatic phenomenon. However, there is strong experimental evidence that this is related to the dual role of the magnetic ion Gd$^{3+}$, which both provides a large local moment and carriers for conduction, similar to the DMS systems like (Ga, Mn)As.

The model system of this class of materials is $a$-Gd$_x$Si$_{1-x}$ films prepared by $e$-beam coevaporation [32]. $a$-Gd$_x$Si$_{1-x}$ undergoes a zero-field $M$-$I$ transition at a critical concentration $x_c$~0.14. Near $x_c$, an enormous negative MR was found (-10$^5$ at 1K), which was used to drive an insulating sample metallic with a critical field $H_c$ [47]. Spin-glass freezing is found in $a$-Gd$_x$Si$_{1-x}$ and it appears to be due to a carrier-mediated RKKY-type interaction. Based on low field $\chi(T)$ measurements, the Gd effective moment is suppressed near the $M$-$I$ transition (below the value for free Gd ion [48]). Magnetization is only 0.6 of the saturation value at $H$ as high as 250 kOe, comparable to a temperature scale of 120 K for $J=7/2$ and $g=2$ [49]. This indicates very strong AFM Gd-Gd interactions are present in this material, but are balanced by equally strong FM interactions, giving a very small Curie-Weiss temperature in the paramagnetic state.

For the metallic samples, the high-$T$ conductivity has a linear $T$ dependence attributed to weak localization and the low-$T$ conductivity has a $T^{1/2}$ dependence attributed to electron-electron interactions [47]. The latter corresponds to an $E^{1/2}$ dependence of the DOS [50] measured by electrical tunneling spectroscopy. When tuned through the $I$-$M$ transition by applying a magnetic field, the DOS at the Fermi surface has a smooth transition from the insulating side with a fully developed Coulomb gap to the metallic side with Coulomb interactions. Both con-
ductivity $\sigma$ and DOS at $T \to 0$ K go to zero at the transition but with different functionalities: the DOS is proportional to $(H-H_c)^2$ while $\sigma(T \to 0$ K) is proportional to $(H-H_c)$. Infrared (IR) spectroscopy showed that there is a large spectral weight (proportional to $n/m^*$, $n$ is carrier density and $m^*$ is carrier effective mass) loss below the a-Si band gap absorption ($\sim 10000$ cm$^{-1}$) with decreasing $T$, and that it is partially recovered at constant $T$ with increasing $H$. Unusual transfer of the spectral weight also occurs in materials with strong electron correlations, such as mixed-valance manganites [5, 51]. Specific heat measurements showed that by increasing the carrier density with fixed Gd concentration, the magnetic contribution to the heat capacity was reduced, indicating weaker magnetic interactions. This is consistent with a reduction in a RKKY-like indirect exchange interaction mediated by conduction electrons [52].

A characteristic temperature ($T^*$) in metallic $a$-Gd$_x$Si$_{1-x}$ is defined by comparing its $\sigma_{dc}(T)$ with that of a nonmagnetic analog: $a$-Y$_x$Si$_{1-x}$ [53]. With similar doping $x$, $a$-Y$_x$Si$_{1-x}$ and $a$-Gd$_x$Si$_{1-x}$ films have exactly the same $\sigma_{dc}(T)$ at high $T$, but when $T$ drops below $T^*$, $\sigma_{dc}(T)$ of $a$-Gd$_x$Si$_{1-x}$ decreases rapidly with $T$ and falls below $\sigma_{dc}$ of $a$-Y$_x$Si$_{1-x}$. This deviation becomes very substantial at low $T$. The characteristic temperature where the deviation starts is defined as $T^*$, which is a pretty high $T$ scale, much higher than the spin-glass freezing temperature $T_f$. $T^*$ for fixed Gd $x$ was found to decrease with the sample metallicity, either by adding more electrons (increasing Gd $x$ or constant Gd $x$, increasing Y $y$ in ternary samples $a$-Gd$_x$Y$_y$Si$_{1-x-y}$), or by changing the semiconductor matrix (from $a$-Si to $a$-Ge) [53]. This observation suggests the important role of electron screening in this type of materials, and supports the conclusion that these materials are strongly correlated materials.

### 1.4 Summary

In summary, adding spins in semiconductors provides rich phenomena for scientific studies and potential technological applications. Moment-carrier interactions bridge together the fields of magnetism and semiconductor physics. Even in a fairly simple binary material system $a$-Gd$_x$Si$_{1-x}$, astonishing effects such as enormous
negative MR is seen. The study of these materials can thus be very rewarding.

In this dissertation, Gd and Mn as magnetic dopants in group IV amorphous semiconductors are explored. In Chapter 3, properties of \( a\)-Gd\(_x\)Si\(_{1-x} \) prepared by magnetron cosputtering (a quite different deposition technique than \( e\)-beam evaporation used before) are presented. Although sputtered \( a\)-Gd\(_x\)Si\(_{1-x} \) films have quite different film morphology at the 10-nm scale from the \( e\)-beam evaporated films (dense vs columnar), the measured magnetic and magnetotransport properties are almost the same. In Chapter 4 and 5, magnetron cosputtered \( a\)-Gd\(_x\)C\(_{1-x} \) films and Gd-implanted ion-beam deposited tetrahedrally amorphous carbon (\( ta\)-C\(_{1-x} \).Gd\(_x \)) films are presented. Correlation between the physical properties and the microstructure of the \( a\)-C matrices are discussed. Finally, in Chapter 6, the transition metal Mn is used as the dopant in \( a\)-Si, in analogy to the \( a\)-Gd\(_x\)Si\(_{1-x} \). However, the local Mn moment is found to be quenched and thus no large MR is found. This is because only a small fraction of doped Mn are found to be in the Mn\(^{2+} \) states with \( 5 \mu_B \) local moment. The majority of the Mn are in nonmagnetic states, presumably due to formation of an impurity band as indicated by X-ray absorption measurements. The existence of itinerant states in insulating samples is explained by Anderson localization in this strongly disordered amorphous material. States in this band are localized due to disorder when \( x \leq x_c \), and delocalized when \( x > x_c \). These localized itinerant states have no magnetic moment.
Survey of Experimental Methods

The goal of this chapter is to briefly discuss the experimental fundamentals which have been utilized for the projects in this dissertation. This chapter introduces a variety of thin film material growth methods, materials characterizations and physical property measurements.

2.1 Thin Film Growth

Non-equilibrium processes can be used to stabilize metastable phases that are very hard to achieve by bulk synthesis methods. Condensing thin film materials from the vapor phase onto a substrate held at low temperatures is one way to achieve non-equilibrium material growth. Thin film deposition methods with advances in modern vacuum science and technology have provided researchers with a great variety of tools for high quality thin film growth. CMR in oxide films and LMR in Bi films discussed in the previous chapter are two excellent examples of how advancement in thin film growth technique leads to the discovery of these MR effects with much larger magnitude than previously observed in their bulk counterparts.

2.1.1 e-beam Evaporation

e-beam evaporation uses deflected high-energy electron beam to thermally heat and evaporate the source materials in a copper liner. By controlling the position
of the e-beam spot (using X-Y sweep coils) and the power of the e-beam current, one can easily control the melting profile of the source materials and the deposition rate. Compared with thermal evaporation with just resistive heating (usually with tungsten baskets or crucibles), e-beam evaporation has much better control and much better purity (no alloying problem with tungsten). This is important for coevaporation of multiple sources to achieve a uniform off-stoichiometric film composition. The pressure during deposition is kept very low, usually in the ultra-high vacuum (UHV) or high vacuum (HV) range (<10^{-9} Torr), thus the mean free path (MFP) of deposited atoms are long and almost no gas phase collision occurs. UHV conditions guarantee that the impurity flux from the residual gas in the background (usually consists of unwanted species like N\textsubscript{2} and H\textsubscript{2}O) is negligible compared with the deposited molecular beam flux, since the flux Φ in molecules/cm\textsuperscript{2}-sec from the residual gas phase has the following pressure dependence:

$$\Phi = 3.513 \times 10^{22} \frac{P}{\sqrt{MT}}.$$  \hspace{1cm} (2.1)

where $P$ is the residual gas pressure in Torr, $M$ is the molecular mass in amu. From Eq. 2.1, one can estimate the formation time $t_m$ of one monolayer (10\textsuperscript{15}/cm\textsuperscript{2}) of adatoms:

$$t_m \sim 2 \times 10^{-6} \frac{1}{P}.$$ \hspace{1cm} (2.2)

where $t_m$ is in sec. If only a specific type of molecule in the residual gas is important, $P$ is then the partial pressure of that molecule. Eq. 2.2 tells us at $P \sim 10^{-9}$ Torr, a monolayer forms in $\sim 2000$ sec (half an hour) assuming the adatom has a unity sticking coefficient (no desorption once stuck). Typical lab growth rate can be a monolayer/sec and means impurity level of 1/2000. Considering that the sticking coefficient is always less than unity and the pressure is better than 10\textsuperscript{-9} Torr under UHV conditions, the impurity level can be even lower than this rough estimation. Such a low impurity level is essential for the growth of high quality semiconductor materials.

The arrival kinetic energy ($E_k$) of deposited atoms at the substrate is approximately the thermal energy ($k_B T$) gained from the melting source, which is $\sim 0.1$ eV for most materials. $E_k$ directly determines the mobility of the adatoms on surface, thus greatly affects the film growth mechanism. Due to the small $E_k$ and
the well-controlled growth rate, e-beam evaporation is considered as a very “gentle” process good for epitaxy. Substrate temperature can be raised to increase the surface as well as the bulk diffusion to achieve equilibrium phases, or can be kept low to promote non-equilibrium phases such as the amorphous structure. e-beam evaporation is one of the best methods for preparing the elemental semiconductor thin films, such as Si and Ge, due to its ease of control, high power and ultra-high vacuum (UHV) environment (less impurities).

2.1.2 Magnetron Sputtering

Sputtering deposition is a more energetic deposition method compared with e-beam evaporation. Using Ar as the working gas, an Ar plasma is initiated by applying a high negative voltage. Secondary electrons generated in this process help to sustain the plasma. Positive Ar ions are attracted by the negative-biased target electrode (the cathode), and arrive at the target material with high kinetic energies (∼100 eV, depending on the applied voltage at the cathode). Through the momentum transfer process between the Ar ion and the target material, the target atom not only gains enough energy to escape, but also possesses an $E_k$ which can be as high as tens of eV (compared with typical values for evaporation ∼0.1 eV). $E_k$ in this range greatly promotes surface diffusion and has the similar effect as increasing the growth surface temperature such as in ion-beam-assisted deposition. The $E_k$ of the adatoms can be tuned by changing the Ar pressure thus changing the MFP. Thus sputtering provides an important extra process parameter for controlling the thin film growth. A simplified pressure dependence of the MFP is:

$$l_{MFP} = \frac{5 \times 10^{-3}}{P}.$$  \hspace{1cm} (2.3)

where $l_{MFP}$ is the MFP distance in centimeter and $P$ is the gas phase pressure in Torr. Traditional diode sputtering system requires tens of mTorr in order to sustain the plasma. This is because there is no confinement of the dissociated species and the plasma is everywhere in the chamber. This causes problems such as sputtering of unwanted surfaces (thus introduce impurities) and electron heating of the growing film. Under this high sputtering pressure condition, $l_{MFP}$ is small.
and sputtered atoms are thermalized before reaching the substrate. With the development of magnetron sputtering, where magnets behind the sputtering target are used for confining secondary $e^-$'s trajectories near the target surface, the Ar plasma can be sustained under Ar pressures as low as $\sim0.5$ mTorr. Giving that typical target to substrate distance is $\sim10$ cm, gas phase collisions are only in the order of 1. Therefore, most of the initial $E_k$ of the sputtered atoms can be preserved for film growth that needs higher surface mobility than the thermally evaporated atoms have. This usually leads to a dense film structure with compressive stress, as opposed to columnar film structure with tensile stress often found in thermally evaporated films.

Magnetron sputtering is best for deposition of conductors, such as metals. For insulators and semiconductors, radio-frequency (rf) sputtering is needed to compensate the target charging effect thus deposition rate is poor and sustaining the plasma is more challenging. The deposition rate generally increases linearly with the sputtering power and allows a wide range of control.

2.1.3 Ion Beam Deposition and Implantation

In ion-beam deposition (IBD) the deposited atoms are ionized and accelerated in an electrical potential $V$ under HV conditions. Therefore, the deposited atom $E_k$ can be tuned between 10s of eV up to 1000s of eV. Surface growth is no longer a valid model to describe the growth mechanism when $E_k$ becomes large. Such an energetic method is essential for preparing some high-temperature high-pressure phases. One example is the preparation of tetrahedrally amorphous carbon (ta-C), which has predominant $sp^3$ C-C bonds as in the diamond phase. The optimum energy window to grow ta-C was found to be $\sim100$ eV [54], which can not be achieved by $e$-beam evaporation or sputtering.

In the ion implantation process, the implanted source material is ionized and accelerated in a similar way as for the IBD process, but $E_k$ is even higher ($>10$ keV) in order to drive the ions deep into the matrix. One unique feature of ion implantation is that the film growth occurs well beneath the substrate surface. Thus ion implantation is often used for doping [55].
Precise numbers of deposited atoms and a specific dose can be easily achieved by IBD and ion implantation, respectively, since the electrical charges of the ions can be easily counted by collection in a Faraday cup.

2.2 Materials Characterization

2.2.1 High Resolution Transmission Electron Microscopy (HR-TEM)

High Resolution Transmission Electron Microscopy (HR-TEM) is a very important research tool for thin film microstructure and nanoscience studies. Advances in modern electron microscopy have achieved atomic resolution both structurally and chemically [56].

A transmission electron microscopy (TEM) image forms in two successive steps. First, the high-energy incident electrons are scattered both elastically and inelastically due to various interactions with the atoms when passing through the studied materials. Second, the electron wave function coming out at the exit surface is transmitted through different lens systems (objective lenses, intermediate lenses and magnifying lenses etc) to form the final image. The inelastically scattered electrons can be utilized for the chemical analysis, such as the electron energy loss spectroscopy (EELS). The elastically scattered electrons can be utilized for the final high-resolution lattice and atomic imaging.

Different types of image contrast can be chosen to obtain different materials information. For high-resolution bright-field phase-contrast imaging, the interference pattern due to the relative phase difference between the transmitted and the diffracted electrons near the optic axis is used for imaging. For amplitude-contrast imaging, all of the diffracted electrons and a significant amount of scattered electrons are excluded for imaging. The image contrast comes from local differences in the electron scattering. Diffraction contrast is usually caused by defects in crystalline materials which causes local variation of diffraction conditions due to the bending of crystal planes. In a scanning TEM (STEM) setup, a dark-field mode (only one diffracted beam is selected compared with all in the bright-field
mode) called high-angle annular-dark-field (HAADF) can be used to increase the so-called Z-contrast due to the \(Z^2\) dependence of the large-angle thermal diffuse (Rutherford) electron scattering. Therefore, the contrast for imaging heavy atoms is greatly enhanced at a cost of a significant drop of the overall image intensity due to the partially-allowed transmission of the diffracted beams.

Selected-area diffraction (SAD) mode is widely used to obtain information on selected small sample regions. This is realized by inserting an aperture at the first intermediate image plane to define the sample area which is allowed to contribute to the image. Crystal structure and lattice spacing information can be obtained for sample areas as small as a few thousand angstroms across. Sharp spot patterns, concentric ring patterns, and broad, diffuse ring patterns corresponds to the single crystalline, polycrystalline and amorphous regions, respectively.

### 2.2.2 Ion Beam Analysis

Rutherford backscattering (RBS) is one of the most used ion beam analysis techniques. RBS is a non-destructive method to determine important film information including the composition and the atomic areal density. Typical RBS spectroscopy utilizes \(^4\)He\(^{2+}\) with an incoming kinetic energy \(E_0=2\) MeV. The backscattering yield \(Y\) is proportional to:

\[
Y \propto \left( \frac{Z_1 Z_2}{E_0} \right)^2 \cdot \Omega \cdot I_0 \cdot (Nt).
\]  

(2.4)

where \(Z_1\) is the He atomic number and \(Z_2\) is the atomic number for the element of interest, \(\Omega\) is the solid angle of the collector, \(I_0\) is the \(^4\)He\(^{2+}\) incident flux, \(N\) is the number density (in atoms/cm\(^3\)) and \(t\) is the film thickness, so \((Nt)\) is the areal density, which is the parameter directly obtained from RBS. If \(t\) is known, then film number density \(N\) can be calculated, or vice versa. \(^4\)He\(^{2+}\) loses its kinetic energy when goes through the film. This leads to the broadening of the RBS spectrum. The width of the spectrum provides element-specific film thickness information. Due to the same reason, elements in buried layers will have their spectra shifted to lower energies.

Eq. (2.4) shows that low \(Z\) elements, such as carbon and oxygen, have much smaller yields compared with high \(Z\) elements, such as Gd. Moreover, the backscat-
Figure 2.1: (Color) (a) RBS spectrum for an a-C:H sample with Ag capping; (b) Hydrogen forward scattering (HFS) spectrum for the same sample. H yields were calibrated with a Kapton film.
tering energy for lighter elements is so low that the signal is convoluted with that from the thick substrate. To resolve this problem, resonance RBS can be used for a specific light element. For example, in order to detect carbon, the $^4\text{He}^{2+}$ energy is tuned to 4.3 MeV, where $^4\text{He}^{2+}$ undergoes a nuclear resonance elastic scattering with C atoms. This greatly increases the backscattering cross-section of C and enhances the C signal by a factor of 10, as shown by the sharp peak in the inset of Fig. 4.2 in Chapter 4. Another example is in Chapter 6. There, O resonance RBS ($E_{\text{Res}}=3.05$ MeV) is used for detecting a surface oxide (Fig. 6.2). Since the resonance scattering only occurs at a very small energy window near $E_{\text{Res}}$, when $E_0$ exactly equals to $E_{\text{Res}}$, O on the film surface undergoes resonance backscattering and gives rise to the $O_{\text{Res}}$ signal as shown in Fig. 6.2. When $E_0>E_{\text{Res}}$, the $^4\text{He}^{2+}$ has to reduce its kinetic energy to $E_{\text{Res}}$ by penetrating a certain depth below the film surface, and then is in the right energy window for resonance backscattering. Thus the existence of O inside the film can be detected (O is often an undesired impurity in semiconductors). In Fig. 6.2, the fact that the $O_{\text{Res}}$ signal decreases when $E_0$ increases above $E_{\text{Res}}$ indicates that only a thin surface oxide layer is formed while no O is present inside the film.

Hydrogen atoms are so light that they are invisible in the backscattering geometry. Instead, H atoms can be knocked out of the film by $^4\text{He}^{2+}$ in a forward scattering setup, known as hydrogen forward scattering (HFS). This can be used to determine the H concentration in hydrogenated films. The HFS samples need to be capped (by a thin Ag or Al layer) in order to separate the H signal in the sample from the signal of any hydrocarbon contamination on the film surface. The hydrogen yields can be calibrated with a Kapton thin film. Fig. 2.1 shows an example of using HFS for determination H concentration in an hydrogenated amorphous carbon thin film, which will be discussed more in Chapter 4.

### 2.2.3 Raman Spectroscopy

Raman spectroscopy measures the phonon vibrations in materials; these vibrations can be associated with bonding and structure information. In particular, it is used in this dissertation to obtain information about the amorphous carbon’s $sp^2$
Figure 2.2: (Color) Raman spectra for pure carbon thin films with different structures. From the top: CVD micro-crystalline diamond (MCD), CVD nano-crystalline diamond (NCD), IBD $ta$-C, 20% hydrogenated sputtered $a$-C, 4% hydrogenated sputtered $a$-C and hydrogen free sputtered $a$-C.
and $sp^3$ bondings [57]. Detailed information of the local bonding configuration can be deduced, such as the $sp^2$ carbon ring, the $sp^2$ carbon chain and the $sp^3$-bonded centers. Disordered carbon systems have two Raman active modes when excited with a 488-nm excitation laser: one is at 1580 cm$^{-1}$ of $E_{2g}$ symmetry, labeled $G$; the other is at 1350 cm$^{-1}$ of $A_{1g}$ symmetry, labeled $D$. Both modes correspond to the $sp^2$ bonding scheme, but are related to different bonding configurations of the $sp^2$ sites. The $G$ mode is the stretching vibration of any $sp^2$-bonded sites, whether in chains or in aromatic rings, while the $D$ mode is the collective breathing mode of the $sp^2$ sites in six-member graphitic rings, thus only related to disordered graphitic sites. Depending on the $sp^2$ fraction and arrangement (whether in chains or in graphitic rings), the relative peak intensities, the peak positions and the peak widths of the two Raman modes will change accordingly [54]. At the excitation wavelength used in the present work, $sp^3$ modes are invisible but indirect information can be obtained. The Raman vibration mode specific to $sp^3$ sites is visible at $\sim$1050 cm$^{-1}$ but must be excited by an ultraviolet (uv) laser [58].

Carbon bonding information, specifically the $sp^2$ and $sp^3$ fractions, can be obtained by analyzing the $G$ peak position, $I_D/I_G$ ratio and peak width, based on the three-stage model proposed in Ref. 59. As we have discussed, Raman spectra are very sensitive to the carbon structure and morphology, thus a very powerful fingerprint characterization technique for carbon materials as shown in Figure 2.2. Detailed applications will be shown in Chapter 4 and 5.

### 2.2.4 X-ray Absorption Spectroscopy (XAS)

In Chapter 6, X-ray absorption spectroscopy (XAS) is used to probe the electronic structure of the Mn dopant in $a$-Mn$_x$Si$_{1-x}$ thin films. XAS measures element-specific absorption edges at characteristic energies associated with the excitation of electrons from the occupied core-level states to the unoccupied outer-level states. For example, the Mn $L$-edges absorptions $L_2$ and $L_3$ peaks correspond to electronic transitions from the occupied Mn $2p_{1/2}$ and $2p_{3/2}$ states to unoccupied Mn $3d$ states, respectively. The reverse relaxation process back to the ground states generates fluorescence photons or electrons (including Auger $e^-$ and secondary $e^-$),
Figure 2.3: XAS data of Mn $L_3$ and $L_2$ edges for Mn in different local environment. (a) mixed MnO and Mn$_2$O$_3$ powder; (b) Mn$_3$O$_3$ powder; (c) MnO$_2$ powder; (d) Mn in a-Ge film; (e) sputtered Mn metal film. The oxide powders are commercially available.
which can be detected by a photon diode in the fluorescence yield (FY) mode or an electrometer in the total electron yield (TEY) mode. Since photons have longer mean free path than electrons in solids, the FY mode is more sensitive to the bulk film properties (∼10 nm) while the TEY mode is more surface sensitive (<4 nm).

Analysis of the XAS spectral structure includes the peak and sub-peak shapes and positions. More detailed analysis includes the branching ratio (defined by $\int L_3/(\int L_2 + \int L_3)$) and splitting energy between sub-peaks. If the final electronic states are still atomic-like, simulations can be done by standard atomic multiplet programs [60], with the crystal field splitting energy (corresponds to the fitting parameter $10Dq$), the site symmetry and the charge state as free adjustable parameters. Since XAS probes the local electronic structure, spectra of mixed states, such as different valence states for a transition metal, can be treated as linear superposition of individual ones. Thus composition of different electronic states (valences) of the studied element can be extracted. XAS is widely used for the study of mixed-valence manganites, such as La-Ca-Mn-O [61,62]. Detailed examples of XAS in this dissertation are shown in Chapter 6.

The XAS spectra in this dissertation were taken at the Advanced Light Source (ALS) beam line 6.3.1, Lawrence Berkeley National Lab. The energy resolution is of ±0.2 eV. The drift of the X-ray energy as a function of time is also found to be small ∼±0.1 eV. Signals were collected in the TEY mode. Since TEY is very surface sensitive as discussed, all measured thin film samples are capped with 2∼4 nm Al and stored in a vacuum desiccator to avoid oxidation. Al is known to form a self-limiting oxide layer thus protecting the underlying films. Also, at the Mn $L$ edges absorption energy ∼640 eV, The X-ray absorption coefficient of Al is about order of magnitude smaller than that of the Mn.

### 2.3 Materials Physical Properties

#### 2.3.1 Magnetization

Magnetization measurements of a thin film are done with a superconducting quantum interference device (SQUID) magnetometer manufactured by Quantum
Design. The SQUID pick-up coils are very sensitive to the changes of magnetic flux due to the movement of a dipole moment (manufacture specification $\sim 10^{-8}$ emu), which gives a measurable voltage signal. This setup provides us with a 70 kOe dc magnetic field and a wide temperature range of 2-400 K. Magnetization (both dc and ac) as a function of magnetic field $H$ and temperature $T$ can be measured.

$M(T)$ can be done by zero-field cooling (ZFC), where the sample is first cooled in zero field and then the magnetization is measured on heating in a dc $H$ field, or by field cooling, where the sample magnetization is measured in a dc $H$ field during cooling. In the paramagnetic states, ZFC and FC $M(T)$ curves are identical and usually follow the Curie-Weiss (CW) law based on the Weiss mean-field theory:

$$\chi(T) = \frac{A}{T - \theta},$$

(2.5)

$$A = \frac{Np^2_{\text{eff}}\mu^2_B}{3k_B}.$$  

(2.6)

where $\theta$ in K is the CW temperature and $A$ is the CW constant. Splitting between ZFC and FC curves occurs when magnetic interactions start to dominate below a transition temperature and the sample magnetization starts to depend on history.

Thermoremanent moment (TRM) measurement are often used to characterize spin glass or antiferromagnetic phases by detecting uncompensated spins. For TRM measurements, the sample is first cooled in a large magnetic field (70 kOe in our system), and then measured on heating in zero field.

For free magnetic ions, the field- and temperature-dependence of magnetization is described by the Brillouin function:

$$B_J(x) = \frac{2J + 1}{2J} \coth \left( \frac{(2J + 1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right).$$

(2.7)

The magnetization is given by:

$$M = ngJ\mu_B B_J(x).$$

(2.8)

where $x \equiv gJ\mu_B H/k_B T$, $n$ is the number density of magnetic ions and $g$ is the $g$ factor (the spectroscopic splitting factor). Eq. 2.8 is known as the Curie-Brillouin law. When $x \ll 1$, Eq. 2.8 can be reduced to the Curie law [36].

$$\chi = \frac{A}{T},$$

(2.9)
Eq. 2.9 and Eq. 2.5 are different by the CW temperature $\theta$ in the denominator. While the Curie law describes the paramagnetic behavior of truly free magnetic ions, the CW law describes the paramagnetic behavior above magnetic ordering temperatures, such as for a ferromagnet above its Curie temperature $T_C$. In the paramagnetic states for a ferromagnet, although the large thermal fluctuation destroys the spontaneous magnetic ordering, the internal interaction that tends to align the moment are still there. In the mean field approximation, this internal interaction is treated as an exchange field (the Weiss field), a virtual magnetic field which is proportional to the sample magnetization. $\theta$ in Eq. 2.5 then is a measure of the strength of this exchange field. For simple ferromagnets with a single exchange interaction, $\theta$ agrees with $T_C$ fairly well. For magnetic systems with more than one exchange strength, such as an antiferromagnet which has different exchange fields for each antiparallelly aligned magnetic sublattice, $\theta$ does not always equal $T_N$. For materials with spin-glass magnetic ground states, $\theta$ is usually small due to the competition between AFM and FM interactions that lead to the spin frustration below the spin glass freezing temperature $T_f$.

As an approximation, the CW law work surprisingly well for $T \gg T_C$. The assumed exchange field is an approximation of the quantum mechanical exchange interaction, which is related to the overlap of electron wave functions of two magnetic ions. The energy change associated with this is called the exchange energy. Fundamentally, this energy change is originated from the Pauli exclusion principle and the electrostatic force.

Measuring the thin film magnetization as a function of temperature and magnetic field is essential for this dissertation work and examples can be found from Chapter 3 to Chapter 7.

### 2.3.2 Transport and Magneto-transport

Determining the sample conductivity can be deceivingly simple. The well-known four-point probe method we have adopted can help to get rid of the lead contact resistance. However, it is still essential to get a good ohmic contact in order to reduce the parasitic capacitances. Since we are measuring the dc trans-
port properties, capacitive components in the measurement circuit is especially not desirable. They could delay the circuit equilibrium time and lead to incorrect values. With good contacts and fast circuit response time (small RC time constant), one can source a dc current and switch its polarity from the two outer leads, while measuring the dc voltage between the two inner leads. The sample resistance equals:

\[ R = \frac{V_+ - V_-}{2I} \]  

(2.10)

where \( V_+ \) and \( V_- \) are the measured voltages corresponding to the two different current polarities. This helps to get rid of any zero bias offset due to instrumental artifacts, non-ideal contacts, any thermoconductivity or photoconductivity and so on. At low temperatures, samples on the insulating side of the \( M-I \) transition become very resistive (\( R > 10^8 \) \( \Omega \) for a typical 100 nm-thick film) and behave as a poor dielectric. The measuring circuit inevitably picks up a capacitive component, leading to a large \( RC \) time constant. Now, a slow \( V-I \) sweep is necessary to confirm the ohmic behavior. Sample resistance can be obtained by fitting to the linear part of the \( V-I \) curve. Temperature fluctuations, fast current sweeps, bad electrical contacts and the sample self-heating are among the many causes for the non-linear behavior in \( V-I \) characteristics.

To obtain reliable \( \sigma_{dc} \), sample geometry needs to be known. The lateral dimensions can be lithographically defined. The sample thickness (\( t \)) can be controlled in situ by quartz crystal thickness monitors and measured after deposition by X-ray low-angle reflection (for \( t < 60 \) nm), atomic force microscopy (for 10 nm< \( t < 500 \) nm) and profilometer (for 50 nm< \( t < 2 \) \( \mu \)m). For the latter two methods, one needs a sharp film step-edge. The uncertainty in \( t \) should be controlled within 10% and is usually the dominant error in \( \sigma_{dc} \).

Magneto-transport is done by setting the above transport setup in a dc magnetic field. By changing the relative orientation of the \( H \) field and the \( E \) field, as well as their orientations relative to the film plane, it is possible in many cases to distinguish different physical origins for the measured MR according to its sign, the magnitude and the orientation dependence of the MR as discussed in Chapter 1 Section 1.3.
2.4 Summary

This chapter provides an overview of the major scientific tools and measurement techniques which are essential for magnetic semiconductor thin film studies. Basic theories and operational principles have been introduced. All these techniques have been directly utilized for projects in this Ph.D dissertation. Detailed applications for each tool and technique will appear in the following chapters for different material systems.
3

Growth and microstructure dependence of $a$-$\text{Gd}_x\text{Si}_{1-x}$ films

A comparison of the electronic and magnetic properties of amorphous $\text{Gd}_x\text{Si}_{1-x}$ ($a$-Gd-Si) thin film alloys prepared by different growth techniques (e-beam evaporation and magnetron sputtering) is reported. High-resolution cross-sectional transmission electron microscopy (HR-XTEM) and Rutherford Back Scattering (RBS) show that the material microstructure is highly dependent on deposition method and growth conditions. Electron-beam-evaporated films have columnar microstructure (column width $\sim$10 nm) while magnetron-sputtered films prepared at low argon partial pressure are featureless. However, the dc conductivity, magnetoresistance and $M(H,T)$ properties of the films are totally independent of this difference in microstructure at the length scale of 10 nm. RBS shows that the films have the same overall atomic number density, independent of Gd incorporation, for a wide range of doping concentrations (up to 18 at.%), and HR-XTEM shows a dense, homogenous and amorphous phase with no clustering at the atomic level. The independence of properties from the nanoscale microstructure strongly argues that the magnetic moment and charge carrier behavior observed previously are a result of fundamental interactions at the atomic level. Films sputtered at high argon pressure are less dense and have an open columnar microstructure which leads to fast degradation of film properties due to massive bulk oxidation.
3.1 Introduction

Magnetic rare-earth-doped amorphous semiconductors have strong magnetic moment and carrier interactions, which lead to remarkable magnetic, transport and magneto-transport properties. Previous studies documenting amorphous Gd$_x$Si$_{1-x}$ ($a$-Gd-Si) films prepared by $e$-beam coevaporation can be found in the literature [32, 47, 53, 63]. In these amorphous films, Gd acts as a trivalent magnetic dopant with a half-filled f electron shell. Gd provides both transport electrons as well as a large local magnetic moment: $J=S=7/2$, in the amorphous semiconductor matrix. This combination of high carrier density and large magnetic moment concentration has significant consequences for the electronic properties, including a concentration and magnetic-field-tuned metal-insulator (M-I) transition [47], a concentration-dependent characteristic temperature ($T^*$) [53] at which the interactions between local moments and electrons turn on (leading to enormous magnetoresistance below $T^*$) [32], and universal concentration and magnetic-field-tuned scaling of the $M$-$I$ quantum phase transition [63]. There are strong similarities between this system and the widely studied dilute magnetic semiconductors (DMSs), such as Ga$_{1-x}$Mn$_x$As and the perovskite manganites. In all of these systems, there is evidence for interactions between the magnetic dopants and the charge carriers. Moreover, coupling between the intrinsic positional disorder of the magnetic dopant and the crystalline lattice structure of the matrix has been suggested to play an important role in the DMS systems. Amorphous Gd-Si films have a large structural disorder compared to their crystalline counterparts.

Whether these electronic properties are associated with the specific microstructure of the amorphous matrix is unknown. Quantitative theoretical descriptions of the highly disordered amorphous materials are not as well defined as their crystalline counterparts due to the loss of periodic structure. As with crystalline materials, a complete description and understanding of the physical properties of the amorphous material ultimately depends on knowledge of the structure. Being amorphous, the films can exhibit a wide variety of short range order and nanoscale microstructure, which could lead to distinctive physical properties. The atomic-level arrangement, microstructure, and thus often the film properties are strongly
dependent on deposition methods and conditions.

Electron-beam (e-beam) evaporation and magnetron sputtering are two widely used and very different deposition methods in thin film technology. One of the major differences between the two is the incident energy of adatoms and the consequent growth kinetics. For e-beam evaporation, the kinetic energy of adatoms is obtained from the thermal energy at the evaporation source, usually a fraction of 1 eV. For magnetron sputtering, the kinetic energy is obtained from momentum transfer between the high-energy working-gas atoms (usually Ar atoms with hundreds of eV) and the target atoms. The sputtered target atoms usually have initial kinetic energy \( \sim 10-50 \) eV and the reflected neutral Ar atoms also have significant energy [64,65]. These high-energy atoms play an important role in compacting the film as it grows, under the condition that they can reach the substrate without significant energy loss due to thermal collisions with the background gas species. The kinetic energy of these atoms can be reduced by increasing the background pressure. This provides magnetron sputtering with a significant control parameter: namely, the background gas pressure. At low substrate temperature, meaning low compared to the melting temperature \( (T_m) \) of the deposited materials [for most metal and semiconductor materials, room temperature (RT) is sufficiently low], e-beam-evaporated films including amorphous alloys usually have columnar microstructure associated with tensile stress [66,67]. The more energetic adatoms in magnetron sputtering have more surface mobility, which helps to relax the tensile stress typically observed in thermally evaporated films grown on substrates at low temperature. At low argon pressure, when the energetic sputtered target atoms reach the substrate without significant thermalizing from gas-phase collisions, large compressive stress is found. A transition from compressive to tensile stress with increasing argon pressure has been reported in many sputtered material systems, associated with increasing thermalization of the energetic atoms [68–73].

For the magnetically-doped amorphous semiconductor system studied here, the atomic environment is key to understanding the underlying physical properties. In particular, it is crucial to understand whether the remarkable magnetic and magneto-transport properties are dependent on microstructural details. In this work, we prepared \( a-\text{Gd-Si} \) films by magnetron sputtering at different argon
pressures, which lead to different film microstructure. We report the transport and magnetic properties of the sputtered films and directly compare them to films prepared by e-beam evaporation. Our effort is aimed at reproducing the unique electronic and magnetic properties of e-beam-evaporated a-Gd-Si films by optimizing the sputtering growth conditions, and also to investigate whether differences in microstructure of the sputtered films will limit the reproducibility of these material properties.

3.2 Experiment Details

Details regarding the preparation of the e-beam-evaporated films have been described previously [48]. The magnetron-sputtered a-Gd-Si films were prepared in an AJA magnetron sputtering system by cosputtering from individual high purity Gd and Si targets. The base pressure prior to deposition was better than $8 \times 10^{-8}$ Torr with a liquid nitrogen cold trap. Films were sputtered at two different argon pressures: 2 mTorr and 6 mTorr. Within each set, one film was capped with a 250 Å amorphous Si (a-Si) layer. The electrical conductance was checked as a function of time after removal from the vacuum to test for film stability. The film composition and areal density (atoms/cm$^2$) were measured by Rutherford backscattering (RBS). Together with film thickness as determined via a Nanopics AFM profilometer, we extracted the atomic number density (atoms/cm$^3$) of the films. High-resolution cross-sectional transmission electron microscopy (HR-XTEM) and energy-dispersive spectroscopy (EDS) were used to assess the film microstructure and to verify film composition. The impurity level, specifically the oxygen content, was analyzed using oxygen-resonance RBS spectra. The temperature and magnetic field dependence of electrical transport, magneto-transport and magnetization were measured. Further details about the experiment setups are described elsewhere [47, 48, 74].
Figure 3.1: XTEM micrographs for an (a) e-beam-evaporated sample, (b) sputtered sample prepared at 2 mTorr, (c) sputtered sample prepared at 6 mTorr. Note the differences in film morphology. Insets for each are HR-XTEM micrographs.
3.3 Materials and Structural Characterization

A low magnification XTEM micrograph for an e-beam evaporated film shows columnar nanoscale microstructure with an average column diameter $\sim 10$ nm [Fig. 3.1(a)]. Low magnification XTEM micrographs for the sputtered films show quite different microstructure, depending on the sputtering pressure. The film sputtered at 2 mTorr does not show columnar microstructure [Fig. 3.1(b)]: instead, the film morphology appears featureless and homogenous. The film sputtered at 6 mTorr Fig. 3.1(c) shows columnar nanoscale microstructure with an average column diameter also $\sim 10$ nm. At high resolution, the HR-XTEM micrographs in the insets of Fig. 3.1 show that the atomic microstructure for all of the films is featureless and amorphous, despite the differences in the nanoscale microstructure.

Figure 3.2 shows a plot of the Gd atomic number density $n_{Gd}$ as a function of Gd concentration $x$. The results for the e-beam-evaporated and sputtered 2 mTorr films are identical. A linear fit of the data yields a slope of $(4.90 \pm 0.07) \times 10^{22}$ atoms/cm$^3$. This is the total number density $n_{total}$ (including both Gd and Si atoms) of the a-Gd-Si films, 1.8% less dense than pure crystalline Si $(4.99 \times 10^{22}$ atoms/cm$^3$ at 300 K), but consistent with the measured number density of a-Si films prepared either by e-beam evaporation [23] or by self-ion implantation of crystalline Si (c-Si) [75]. The film sputtered at 6 mTorr has a $\sim 35\%$ lower Gd number density for the same Gd concentration $x$ (as shown in Fig. 3.2). The inset of Fig. 3.2 shows the total atomic number density $n_{total}$ vs. $x$. For a wide range of Gd doping concentrations, $n_{total}$ is independent of $x$ for both the e-beam-evaporated films and the sputtered 2 mTorr films. The $n_{total}$ for the sputtered 6 mTorr film is $\sim 35\%$ below the value for pure a-Si.

The atomic number density result for the e-beam-evaporated films is consistent with the previous x-ray absorption fine structure (XAFS) study [24]. In the XAFS study, the average Si-Si distance was shown to be 2.39Å, only slightly larger (by $\sim 0.04$ Å) than the Si-Si bonding distance measured in pure c-Si or a-Si. The Si-Si coordination number was measured to be 3.7, in excellent agreement with values found for a-Si prepared by self-ion implantation of c-Si and measured by high-resolution radial distribution function (RDF) [76]. The average Gd-Si distance
Figure 3.2: Gd atomic density as function of Gd concentration. Inset shows overall atomic densities of the films in atoms/cm$^3$. The atomic density of pure (crystalline) silicon ($4.99 \times 10^{22}$ atoms/cm$^3$) is marked as a straight line. For reference, the bulk density of pure gadolinium is $3.01 \times 10^{22}$ atoms/cm$^3$. 
was found to be 2.98 Å. All of these values are independent of $x$, from low Gd concentration up to at least $x=18$ at.%, which is in good agreement with the invariant film total number density $n_{\text{total}}$. The large Gd-Si distance found by XAFS indicates severe distortion of the $a$-Si matrix near the Gd atoms [24]. However, strain caused by the distortion is strongly localized near the Gd atoms, since both the average Si-Si bonding distance and the coordination number remain the same as for pure $a$-Si, implying that the amorphous Si structure is highly effective in relaxing local strain.

The identical and invariant total atomic number densities for both $e$-beam-evaporated and sputtered 2 mTorr films indicate that they share the same local environment envisioned as the following; each Gd ion is substituted for a single Si atom in the $a$-Si matrix, with very little structural expansion, despite the significant differences in ionic/covalent radii. Conceptually, starting with a pure $a$-Si structure, one Si atom is replaced with one Gd ion, expanding the first Si coordination shell (large Gd-Si distance measured by XAFS) in order to accommodate the larger ionic size of Gd. However, the second Si coordination shell remains almost unaffected, except for an increase of mean square disorder of the Si-Si inter-atomic distance, as discussed by Haskel et al. [24].

Room temperature (RT) dc conductance ($G_{RT}$) and conductance ratio between RT and 77K ($G_{RT}/G_{77K}$) can be used as benchmarks to monitor the structure stability under ambient conditions. The $G_{RT}$ values of the $a$-Gd-Si films sputtered at 2 mTorr and those grown by $e$-beam evaporation are stable over time (including after a number of years for the latter material) even with no capping layer. For the sputtered film prepared at 2 mTorr argon pressure, $G_{RT}$ changes by less than 5% over 100 h (as shown in Fig. 3.3) and the $G_{RT}/G_{77K}$ ratio changes less than 1.5% for a wide range of film composition and film thickness. The relatively constant values of $G_{RT}/G_{77K}$ suggest that the change in $G_{RT}$ is due to simple geometric changes in the conduction path (such as film thickness or volume reduction), an effect previously seen in annealing studies of $a$-Nb-Si [77]. The slight reduction of conductance over time is very likely due to a self-limiting thin oxidation surface layer, as observed in films prepared by $e$-beam evaporation when this native oxide was used to provide a controllable tunnel barrier for Pb counterelectrodes [50].
Further evidence for the self-limiting oxide comes from the fact that no oxygen was detected in the bulk of the film by RBS oxygen-resonance spectra.

Figure 3.3: Plot of conductance at room temperature ($G_{RT}$) vs time for different samples under ambient conditions. Data are normalized to the first measured value for each sample.

In comparison, films prepared at 6 mTorr show dramatic relaxation of material structure when exposed to air. The $G_{RT}$ is reduced by $\sim 15\%$ over a period of 30 h, as shown in Fig. 3.3. A 250-A $a$-Si capping layer (sputtered also at 6 mTorr) does not prevent this relaxation. On the other hand, the $G_{RT}/G_{77K}$ ratio shows no significant change. RBS and EDS analysis both show significant oxygen content in the films. The degradation of films prepared at 6 mTorr is thus likely to be due to formation of insulating oxides within the film. For sputtered metal films, the microstructure obtained at high sputtering pressures is characterized by tapered crystals separated by open, voided boundaries; these porous boundaries serve as fast diffusion paths leading to massive bulk oxidation [70, 72, 73]. Although this zone model was originally proposed for sputtered metal films with polycrystalline structure, similar sputtering pressure dependence of the film microstructure and
impurity level has also been found for sputtered amorphous alloys, such as Tb-Fe [71], TaBₙ and TaSiₓ [78]. The lower overall number density for the sputtered 6 mTorr films indicates a less dense, open columnar structure. It is interesting to note that our e-beam a-Gd-Si films have an apparently similar columnar microstructure (as seen in the XTEM micrograph in Fig. 3.1), but do not show any oxygen from RBS or degradation of the film properties. We suggest therefore that the substantial differences in the stability of the material electronic properties are linked specifically to changes in atomic structure (measured by the average atomic number density), which is more significant than the columnar nanoscale microstructure.

3.4 Electronic and Magnetic Properties

Figure 3.4 shows the dc conductivity $\sigma_{dc}(T)$ of the a-GdₓSi₁₋ₓ films sputtered at 2 mTorr for various Gd concentration $x$. The monotonic increase of the $\sigma_{dc}(T)$ curves with respect to the Gd doping concentration $x$ indicates the successful electrical doping behavior of Gd in the a-Si as matrix, previously seen for e-beam-evaporated samples. As $x$ spans between 9.9 and 18.0 at.%, the system undergoes a concentration-driven metal-insulator ($M$-$I$) transition at a critical concentration $x_c \approx 14.5$ at.%, as shown in Fig. 3.4(a). In $M$-$I$ transition physics, a metal is defined as its residual dc conductivity at $T \rightarrow 0K$ is finite while an insulator is defined as its residual conductivity at $T \rightarrow 0$ K is zero. The sputtered a-Gd₀ européen Si is very slightly on the insulating side of the $M$-$I$ transition, whereas the $M$-$I$ transition for the e-beam films is at $x_c = 14.0$ at.%, suggesting a small shift in the critical concentration. However this difference is close to the compositional resolution of RBS and may not be meaningful. Figure 3.4(b) shows a direct comparison of two sputtered and two e-beam evaporated films: for similar compositions, $\sigma_{dc}(T)$ is nearly identical.

Figure 3.5 shows $\sigma_{dc}(T)$ for a-Gd₁₄.₅Si sputtered at 2 mTorr in various magnetic fields at low temperature. As previously seen for e-beam-evaporated films, there is a very large negative magnetoresistance (MR), due to interactions between the magnetic moments and the conduction electrons. The fact that the MR stays the
Figure 3.4: (a) $\sigma_{dc}(T)$ for sputtered $a$-Gd-Si prepared at 2 mTorr with different Gd concentrations. The 14.5 at.% sample is just on the insulating side of the $M-I$ transition. (b) $\sigma_{dc}(T)$ for two sputtered samples prepared at 2 mTorr overlayed on data for $e$-beam evaporated samples.
Figure 3.5: $\sigma_{dc}(H, T)$ plotted vs $T^{1/2}$ for a 14.5 at.% sputtered $a$-Gd-Si sample prepared at 2 mTorr for $H=0, 40, 60, 80$ kOe. A very large negative MR is seen in these sputtered samples similar to previously measured $e$-beam samples (Ref. 74).
same even with different microstructure as compared to the e-beam samples is profoundly important, and indicates the unimportance of structure on the 10 nm scale.

Zero-field-cooled (ZFC), field-cooled (FC) and ac magnetic susceptibility $\chi(T)$ for a 13.0 at.% sputtered film prepared at 2 mTorr are shown in Fig. 3.6. The ZFC and FC data were each measured in 100 Oe, after cooling in 0 or 100 Oe fields, respectively. The ac $\chi(T)$ data was measured in a 4-Oe, 135-Hz oscillating magnetic field. Previous work on e-beam-evaporated films (including frequency dependent measurements) has established that spin-glass freezing occurs at low temperature [48]. The data for samples sputtered at 2 mTorr show the same split between ZFC and FC, and a sharp peak in ac $\chi(T)$, as for the e-beam-evaporated films. The $T_f$ is precisely determined by the sharp peak in the ac susceptibility data for the 13 at.% sample and estimated from the splitting temperature between

Figure 3.6: (Color) ac and dc susceptibility for a 13 at.% sputtered $\alpha$-Gd-Si sample prepared at 2 mTorr. dc data measured at 100 Oe after cooling in zero field (ZFC) or on cooling in 100 Oe (FC). ac data measured in a 4-Oe, 135-Hz oscillating magnetic field.
the ZFC and FC dc susceptibility data for the 14.5 at.% sample.

Figure 3.7: (a) $T_f$ vs Gd at.% for e-beam-evaporated and sputtered (2 mTorr) samples. $T_f$ shown without error bar is determined by the peak in ac susceptibility measurement. $T_f$ shown with error bar is estimated from the splitting between the ZFC and FC dc susceptibilities. (b) Effective Gd moment from Curie-Weiss fitting vs Gd at.%.

We plot the concentration dependence of $T_f$ of the sputtered 2 mTorr samples together with the e-beam samples in Fig. 3.7(a). The magnitude and concentration dependence of $T_f$ for the sputtered samples is very close to that of the e-beam-evaporated samples. $T_f$ increases smoothly with Gd doping across the $M-I$ transition, indicating stronger interactions between the Gd moments. This is consistent with the decreasing Gd-Gd spacing. We note that the temperature dependence of the dc conductivity does not show any transition across $T_f$. The lack of features in $\sigma_{dc}$ is due to no peridocially ordered spin states below the freezing temperature, and the frozen disorder is still the major mechanism for local-moment
and conduction-electron scattering. Applying a small magnetic field will “melt” the spin-glass state and increase the sample conductivity, leading to large negative MR as mentioned previously. However, the characteristic temperature $T^*$ ($\sim 75$ K for a 14.0 at.%Gd sample), which is defined as temperature where the magnetoconductance (MG) equals 1% for a metallic sample [53], is much higher than $T_f$, indicating that a strong moment/carrier interactions appear well above the spin-glass freezing temperature. In this work, by comparing the e-beam evaporated and magnetron sputtered samples, we have shown that this amazingly high characteristic temperature is not particularly associated with the 10-nm scale columnar microstructure only found in the e-beam evaporated samples.

In the paramagnetic state above the $T_f$, $\chi(T)$ fitted well with the Curie-Weiss law ($\chi = \frac{A}{T-\theta}$) with Curie-Weiss temperature $\theta \sim 0$ K, as previously found for e-beam-evaporated films, indicating a high degree of frustration and very small net Gd-Gd interaction. The Gd effective moments $p$ (extracted from $A = n_{Gd}p^2\mu_B^2/3k_B$) also agree with the values of the e-beam-evaporated films, as shown in Fig. 3.7(b). The effective moment has a nonmonotonic dependence on Gd concentration, showing a peak near the $M$-$I$ transition with values close to the free Gd moment. Away from the $M$-$I$ transition, $p$ drops significantly, showing suppression of the Gd local moment. Figure 3.8 shows that in $M$ vs $H$ measurements at $T=2$ K and 10 K, the moment of the 13 at.% sample sputtered at 2 mTorr ($T_f = 5.5$ K) is strongly suppressed below the Brillouin function, indicating that the sample is not simply paramagnetic and has large antiferromagnetic interactions which are balanced with equally strong ferromagnetic interactions (leading to very small $\theta$). This can be explained by RKKY interactions between the Gd moments, which has been observed in metallic Gd and GdSi$_2$ samples. Disorder will not damp the strength of the RKKY interaction and presumably only randomizes the phase of the interaction. Again, the same exact effects were observed in e-beam-evaporated films [32]. The sputtered films thus behave magnetically the same as the e-beam-evaporated films, i.e. they are true spin-glasses with indirect RKKY-like Gd-Gd interactions.
Figure 3.8: The magnetization data of a 13 at.% sputtered (2 mTorr) sample are suppressed below the Brillouin function at 7 T, for temperatures both below ($T=2$ K) and above ($T=10$ K) the spin-glass freezing temperature, which is 5.5 K for this sample.
3.5 Conclusion

The dramatic magneto-electronic properties previously observed for \( a \)-Gd-Si prepared by \( e \)-beam evaporation are also found in films prepared by sputtering at low argon pressure (2 mTorr), despite very different microstructure at the 10-nm scale (columnar vs dense and featureless). The magneto-electronic properties are nearly identical, including concentration and field-tuned \( M-I \) transition, large negative MR, spin-glass freezing and an anomalous effective moment with a peak near the \( M-I \) transition. The independence of the unique magnetic and electronic properties on the film morphology at the 10nm scale, though perhaps expected, is experimentally clearly demonstrated. The \( e \)-beam-evaporated films and the sputtered films prepared at 2 mTorr have the same total atomic number density as pure \( a \)-Si. High-resolution cross-sectional TEM micrographs show that at the atomic level the films are amorphous with no clustering or inhomogeneity. Based on XAFS and the measured atomic number density, we propose that the atomic environment of Gd atoms consists of a highly strained first Si coordination shell embedded in a largely relaxed \( a \)-Si matrix. This argues that in this magnetically doped amorphous semiconductor, the strong moment-carrier interaction (which leads to large MR and \( T^* \)) and strong moment-carrier-moment interaction (RKKY-like leading to spin-glass freezing) are only dependent on the local atomic environment around the Gd atoms, which is therefore both intrinsic and fundamental. For the sputtered \( a \)-Gd-Si films prepared at 6 mTorr, low atomic density and open columnar microstructure lead to massive oxidation of the films and significant degradation of the film properties over time.

3.6 Acknowledgement

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The magnetic rare earth element gadolinium (Gd) was doped into thin films of amorphous carbon (hydrogenated $a$-C:H, or hydrogen-free $a$-C) using magnetron cosputtering. The Gd acted as a magnetic as well as an electrical dopant, resulting in an enormous negative magnetoresistance below a temperature ($T'$). Hydrogen was introduced to control the amorphous carbon bonding structure. High-resolution electron microscopy, ion-beam analysis and Raman spectroscopy were used to characterize the influence of Gd doping on the $a$-Gd$_x$C$_{1-x}$(:H$_y$) film morphology, composition, density and bonding. The films were largely amorphous and homogeneous up to $x=22.0$ at.%. As the Gd doping increased, the $sp^2$-bonded carbon atoms evolved from carbon chains to 6-member graphitic rings. Incorporation of H opened up the graphitic rings and stabilized a $sp^2$-rich carbon-chain random network. The transport properties not only depended on Gd doping, but were also very sensitive to the $sp^2$ ordering. Magnetic properties, such as the spin-glass freezing temperature and susceptibility, scaled with the Gd concentration.

### 4.1 Introduction

Amorphous carbon ($a$-C) thin films are amorphous semiconductors with a tunable band gap. Unlike other group IV amorphous semiconductors, such as $a$-Si or $a$-Ge, which have a tetrahedral $sp^3$-bonded random-network matrix, a typical $a$-C film has a mixture of $sp^2$ and $sp^3$ bonding. Changing the $sp^2/sp^3$ ratio tunes
the band gap of a-C between that of diamond (100\% \textit{sp}^3, band gap $E_g = 5.4$ eV) and graphite (100\% \textit{sp}^2, semimetal with $E_g = 0$). Studies of a-C, diamond-like materials and carbon nanotubes have long focused on the superior mechanical properties. However, recent developments in novel electronic and spintronic materials have drawn attention to the electrical, optical and magneto-electronic properties \cite{79}. Room-temperature positive magnetoresistance (MR$\sim$60\%) was found in some magnetically-doped carbon thin films such as Co$_x$C$_{1-x}$ \cite{80} and Ni$_x$C$_{1-x}$ \cite{81}, with granular magnetic particles in an amorphous carbon matrix. Room-temperature positive MR was also reported for non-magnetically-doped (B-doped) polycrystalline diamond thin films (MR$\sim$100\%) \cite{82, 83} and undoped a-C/n-Si (MR$\sim$12\%) two-layer structures \cite{84}. These results suggest potential technological applications of carbon-based thin films for electronics and spintronics applications.

In this work, we have cosputtered a-C and the magnetic rare earth element Gd [a-Gd$_x$C$_{1-x}(:H_y)$] with a wide range of $x$, and studied the magnetic and magneto-transport properties. Gd has a half-filled $f$ electron shell and is trivalent in solids, which gives rise to a large local moment with $J=S=7/2$ and three valence electrons. Previous studies on Gd-doped e-beam co-evaporated amorphous Si have shown strong interactions between the magnetic moments and carriers leading to very large negative MR (e.g., $10^5$ at 1 K), anomalous magneto-optical properties and spin-glass freezing [Refs 32, 47, 53, 63]. The magnitude of this temperature-dependent negative MR below a characteristic temperature ($T^*$) was suggested to depend on electron screening related to the metallicity of the amorphous matrix \cite{53}. Screening is related to the band gap of the host semiconductor materials: narrower band gap corresponding to larger dielectric constant ($\epsilon$) causing more screening and reducing the effective interaction, leading to smaller MR and lower $T^*$. Evidence for this trend was that MR and $T^*$ were smaller for high $x$ and for a-Gd-Ge compared to a-Gd-Si samples \cite{33}. These results suggest that the MR will be larger and occur at higher temperatures for a wider band gap matrix.

One motivation of the present study was to make use of the tunable band gap of a-C, which depends on the $sp^2/sp^3$ configuration, and then to study the magneto-transport properties of this type of thin film.
The inclusion of Gd is shown to have large effects on transport and magnetic properties of the $a$-C(:H) films. The dual roles of Gd in this material lead to strong interactions between the carriers and the magnetic moments, giving an enormous negative MR with strong temperature dependence at low temperature. Gd affects the film transport property by two means: one is by electrical doping and the other is by influencing the carbon bonding structure. Correlations between the microstructure, bonding and physical properties are discussed, and explanations for the properties are provided based on material and electronic structures.

### 4.2 Experimental Details

The $a$-Gd-C(:H) films were prepared by co-sputtering 99.99% pure Gd (dc sputtering) and 99.999% pure pyrolytic graphite (rf sputtering) targets onto floating substrates held at room temperature. Samples for ion-beam analysis were grown on MgO substrates, and samples for magnetization and magneto-transport measurements were grown on insulating amorphous SiN$_x$-covered Si substrates. Various Gd doping concentrations were achieved by controlling the ratio of the Gd/C flux. The base pressure prior to deposition was $\sim 5 \times 10^{-8}$ Torr. The sputtering gas (Ar, 99.995% purity) working pressure was kept low (1.3-2.0 mTorr) in order to increase the mean free path of the sputtered atoms, thus preserving the initial kinetic energy of the sputtered target atoms, which is desirable for decreasing the $sp^2/sp^3$ ratio [54]. At this low sputtering pressure, the mean free path is comparable to the distance between cathode and substrate holder (5 cm), so the number of collisions is $\sim 1$. Therefore, the adatom energy is likely to be preserved near the initial energy [estimated to be 5-10 eV for carbon, based on typical sputtering power/current/voltage values: 250 W/2 mA/900 V (Ref. 85)] gained from the Ar-target atom momentum-transfer process. It has been reported that the concentration of metastable $sp^2$ bonds increases with C atom energy and reaches a maximum in an energy window $\sim 100$ eV [54]. Therefore, typical sputtered $a$-C films are dominated by $sp^2$ sites. In order to suppress the graphitic $sp^2$ bonding and promote the $sp^3$ bonding, we introduced H atoms using a 95%Ar:5%H$_2$ mixture gas at the substrate in addition to pure Ar gas introduced at the Gd and C
targets. Different H incorporation was achieved by fixing the Ar flow rate at 10 sccm and changing mixture gas flow rate or by introducing the pure mixture gas at the targets as the sputtering gas.

Ion-beam analysis including Rutherford backscattering (RBS) with C resonance energy and hydrogen forward scattering (HFS) was used to determine the Gd, C and H concentrations. RBS also provided the atomic areal density from which atomic number density was obtained based on the film thickness as measured by Nanopics atomic force microscope profilometer. High resolution cross-sectional transmission electron microscopy (HR-XTEM) with a JEOL JEM-4000EX was used to determine the film microstructure. Magnetization was measured in a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Magneto-transport measurements were carried out on samples with lithographically defined Hall bar patterns, with the magnetic field applied parallel to the film plane and to the applied current. This geometry leads to effects dominated by interactions with the Gd spin, rather than quantum backscattering.

4.3 Materials and Structural Characterization

4.3.1 High Resolution Electron Microscopy

Figure 4.1 shows typical HR-XTEM images for two samples. For both the hydrogen-free [Figure 4.1(a)] and hydrogenated [Figure 4.1(b)] Gd-doped films, the electron micrographs show dense amorphous microstructure, without any observable clustering or crystallization up to at least 22 at.% Gd. The resulting films were very stable in ambient conditions. The same dense and featureless microstructure was also observed in other sputtered amorphous alloys prepared at low Ar pressure, such as $a$-Gd-Si [25]. By contrast, $a$-Gd-Si showed open columnar structure leading to massive oxidation when sputtered at Ar pressures of $\sim$6 mTorr. These results demonstrate that, under proper conditions, magnetron co-sputtering is an excellent method for obtaining a uniform distribution of dopants in amorphous group IV semiconductors (well above the thermodynamic equilibrium).
Figure 4.1: HR-XTEM micrographs for: (a) sputtered hydrogen free $a$-C with 22.0 at.% Gd ($a$-Gd$_{0.22}$C$_{0.78}$); (b) sputtered hydrogenated $a$-C:H with 15.6 at.% Gd ($a$-Gd$_{0.156}$C$_{0.844}$:H$_{0.20}$).
4.3.2 RBS and HFS

Figure 4.2: (Color) Typical RBS spectrum for Gd-doped H-free amorphous C film with incoming $^4$He energy $E_0$ at 2 MeV; Inset shows RBS spectrum for the same sample with $E_0$ at carbon resonance energy of 4.3 MeV. The □ denotes experimental data and dashed line denotes the simulation fits.

Figure 4.2 shows a RBS spectrum for an $\alpha$-Gd-C sample. The backscattering yield $Y$ is proportional to $(Nt)$, the areal density of the element of interest, where $N$ is the number density (in atoms/cm$^3$) and $t$ is the film thickness. $Y$ is proportional to $Z^2$ so that low-$Z$ elements, such as carbon, have a much smaller yield than high-$Z$ elements, such as Gd. Moreover, the backscattering energy for light elements is low causing the signal to become convoluted with that from the substrate, as seen in the main plot of Fig. 4.2. The $^4$He energy was therefore tuned to 4.3 MeV, where $^4$He undergoes a nuclear resonance elastic scattering with C, thus increasing the backscattering cross section of C and enhancing the C signal by a factor of
∼10, shown as the sharp peak in the Fig. 4.2 inset. This technique measures the film composition with greater accuracy, and is essential to the quantitative study of any Gd concentration-dependent properties, such as the metal-insulator (M-I) transition or film magnetization.

The H content in the a-Gd-C:H films was measured by hydrogen forward scattering (HFS). The HFS samples were capped with a thin silver layer in order to separate the H signal in the sample from the signal of hydrocarbon contamination on the film surface. The hydrogen yields were calibrated with a Kapton sheet. For (95%Ar:5%H$_2$)/Ar gas flow ratio up to 10%, H incorporation was about 5 at.\% (a-C$_{0.95}$:H$_{0.05}$) and was not very sensitive to the ratio. Films were also prepared with the pure mixture 95%Ar:5%H$_2$ gas introduced at the targets, which caused noticeable changes in the bonding structure indicated by Raman spectrum discussed below. The HFS experiment was not performed on these samples, but the H at.% concentration was estimated to be high, ~20 at.% (a-C$_x$:H$_{2x}$) based on Raman spectroscopy in the literature. Despite this high H concentration, the pure a-C:H films were still very scratch resistant, as were the Gd-doped films which had a metallic appearance, showing no visible sign of polymerization.

### 4.3.3 Raman Spectroscopy

Raman spectroscopy is widely used to obtain information on $sp^2$ and $sp^3$ bonding in amorphous carbon films [57]. Disordered carbon systems have two major Raman active modes when excited with a 488 nm excitation laser [86]: one at 1580 cm$^{-1}$ of $E_{2g}$ symmetry, labelled $G$; the other at 1350 cm$^{-1}$ of $A_{1g}$ symmetry, labelled $D$. Both modes correspond to the $sp^2$ bonding, but are related to different atomic arrangement of the $sp^2$ sites. The $G$ mode is the stretching vibration of any pair of $sp^2$-bonded sites, whether in chains or in rings, while the $D$ mode is the collective breathing mode of the $sp^2$ sites in 6-member graphitic rings, thus only related to disordered graphitic sites. Depending on the $sp^2$ fraction and arrangement (whether in chains or in graphitic rings), the relative peak intensity, the peak position and the peak width of the two Raman modes will change accordingly. As $sp^2$ sites evolve towards $sp^3$ sites, the ratio of the $D$ peak intensity to the $G$ peak
Figure 4.3: (Color) Raman spectra for different types of amorphous carbon. Note the evolution of two Raman modes, $D$ peak centered at $\sim 1390$ cm$^{-1}$, and $G$ peak centered at $\sim 1550$ cm$^{-1}$. The $ta$-C was prepared by cathodic-arc deposition, while the other films were prepared by magnetron sputtering.
intensity \((I_D/I_G)\) decreases monotonically [54]. When \(sp^3\) sites start to nucleate, \(I_D\) corresponding to graphitic bonds becomes negligible and the remaining \(sp^2\) sites arrange mainly in chains.

Figure 4.3 shows the Raman spectra for different types of amorphous carbon films, prepared by different growth methods (with and without H). We indeed observe two peaks, one centered at \(\sim 1390\) cm\(^{-1}\) (the \(D\) peak) and the other centered at \(\sim 1550\) cm\(^{-1}\) (the \(G\) peak). As the H concentration in the film is increased, the \(I_D/I_G\) ratio [all peak fitting parameters in this work were obtained by two-Gaussian fit unless stated otherwise. A Breit-Wigner-Fano (BWF) fit for the \(G\) peak and a Lorentzian for the \(D\) peak were also performed. The resulted qualitative trend was exactly the same] decreases, indicating that H opens up the graphitic rings and helps to form \(sp^2\)-bonded carbon chains as expected from the literature. The width (full width half maximum from Gaussian peak fit) of the \(G\) peak, which scales with disorder, is 140-150 cm\(^{-1}\) corresponding to a in-plane correlation length \(L_a\) less than 0.1 nm [54], further assuring the amorphous nature of the matrix. We compare our sputtered \(a-C_{1-y}(H_y)\) samples to a tetrahedral amorphous carbon film (denoted as \(ta-C\), with predominant \(sp^3\)-bonding) prepared by energetic vacuum cathodic-arc deposition (the top curve in Fig. 4.3). A nearly symmetric \(G\) peak with no significant \(D\) peak intensity indicates that there are little graphitic rings but primarily short \(sp^2\)-bonded chains remaining in a \(sp^3\)-dominant \(ta-C\) matrix. Even though the \(sp^2\) sites are a small fraction of the \(sp^3\) sites in \(ta-C\), they still show a large \(G\) peak signal because the Raman cross-section for the \(\pi\) bond is much larger than the \(\sigma\) bond in \(sp^3\). According to the three-stage model proposed by Ferrari [59], the \(sp^2\) fraction of our \(a-C(H)\) is about 90~100\%, typical for films prepared by sputtering. The incorporation of H changes the morphology of the matrix towards more “diamondlike” with less graphitic ring sites and \(sp^3\) sites would have been stablized if a more energetic deposition method was used.

Figure 4.4 shows the Gd influence on the \(a-C(H)\) structure. Although no changes were visible in the HR-XTEM micrographs as the Gd doping was increased (always amorphous and no clustering), there is a dramatic change of the \(sp^2\) bonding order. As shown in Fig. 4.4, the \(I_D/I_G\) ratio increases greatly with Gd concentration at first and then decreases. Starting as a low but broad shoulder
Figure 4.4: (Color) Raman spectra for sputtered Gd-doped (a) $a$-C:H; (b) $a$-C samples with different Gd doping. As Gd doping increases, $I_D/I_G$ increases first and then decreases. $I_D/I_G$ is larger than seen in any $a$-C(:H) film in the literature.
next to the $G$ peak in an undoped $a$-C(:H), the $D$ peak develops into a major Raman peak when Gd concentration increases. In contrast to the H incorporation which makes the $a$-C more “diamondlike”, Gd favors the formation of graphitic $sp^2$ sites. After the $I_D/I_G$ ratio reaches a maximum, it decreases slightly with the Gd concentration. The maximum $I_D/I_G$ value (>4 by BWF+Lorentzian fit) is quite large compared to literature values which are typically $\leq 2.5$ [54], suggesting a large fraction of completely disordered $sp^2$ ring sites. The $G$ peak width decreases after doping but is still broad (90-110 cm$^{-1}$, $L_a \sim$1 nm). These features were observed in both the hydrogenated [Fig. 4.4(a)] and H-free [Fig. 4.4(b)] samples. This structural change has a large consequence on the film transport properties as discussed later.

4.4 Physical Properties

4.4.1 dc Transport

The dc conductivity ($\sigma_{dc}$) and magneto-transport as a function of temperature ($T$) and magnetic field ($H$) was measured for the $a$-Gd-C(:H) alloys. Figure 4.5 shows that $\sigma_{dc}(T)$ for the pure H-free sputtered $a$-C is very small, but greatly increases after Gd doping, thus the electrical doping effect of Gd is obvious. However, $\sigma_{dc}(T)$ increases with Gd doping only up to 11 at.%Gd and then decreases with Gd doping. The 11 at.% H-free sample which has the highest $\sigma_{dc}$ is very close to the M-I transition. $a$-Gd$_x$C$_{1-x}$:H$_y$ behaves and scales similarly. The inset of Fig. 4.5 shows the room temperature conductivity ($\sigma_{RT}$) as a function of Gd at.% for both H-free and hydrogenated samples. The only difference between them is that at similar $x$, $a$-Gd$_x$C$_{1-x}$:H$_{0.2}$ has a much smaller $\sigma_{dc}$ due to the more insulating hydrogenated matrix. The high-$T$ $\sigma_{dc}$ of $a$-Gd$_x$C$_{1-x}$ has a linear slope and negative $d\rho/dT$ (as shown in Fig. 4.5) as is found in other doped disordered semiconductors (Refs. 87, 88). At low $T$, all samples show insulating behavior, with vanishing $\sigma_{dc}$ as $T \to 0$ K. The transport mechanism is that of the variable-range-hopping (VRH) type:

$$\sigma = A \exp \left[ - \left( \frac{T_0}{T} \right)^\nu \right]$$  \hspace{1cm} (4.1)
Figure 4.5: $\sigma_{dc}(T)$ of $a$-Gd-C with different Gd doping. Inset shows $\sigma_{RT}$ as function of Gd at.% for both H-free and hydrogenated samples. A peak in the $\sigma_{RT}$ is visible.
where \( \nu = 1/4 \) if electron-electron interactions are not taken into account [Mott VRH(Ref. 89)], or \( \nu = 1/2 \) if Coulomb repulsion between the carriers is included [Efros-Shklovskii VRH (Ref. 90)]. \( \sigma_{dc}(T) \) at low \( T \) fits \( T^{1/2} \) better than \( T^{1/4} \), similar to \( a\text{-}\text{Gd}_x\text{Si}_{1-x} \) alloys on the insulating side near the \( M-I \) transition [50,74].

Figure 4.6: \( \sigma_{dc} \) (on log scale) for \( a\text{-}\text{Gd}_{0.11}\text{C}_{0.89} \) vs \( T^{-1/2} \) in different \( H \). Lines are fits to VRH with \( \nu=-1/2 \) at low \( T \). Inset shows \( |MR|=|\Delta \rho|/\rho_{0} = \frac{|\rho_{H}-\rho_{0}|}{\rho_{H}} \) (\( H = 70 \text{ kOe} \)) vs \( T \). Below \( T' = 29 \text{ K} \) (indicated by the arrow), MR is large and negative; above \( T' \), MR is small and positive.

Figure 4.6 shows the semilog plot of \( \sigma_{dc} \) as a function of \( T^{-1/2} \), measured in different \( H \). An enormous increase of \( \sigma_{dc} \) in 7 T (\( \sim 10^4 \) at 2.5 K) can be seen. This enormous negative MR is found for both H-free and hydrogenated samples and behaves qualitatively the same. For brevity, results for a \( a\text{-}\text{Gd}_{0.11}\text{C}_{0.89} \) sample were shown to illustrate the two competing MR effects found in both types of films.
One is a positive MR dominant at higher $T$ (up to 100 K). This is a small effect (MR value, defined as $MR = \frac{\Delta\rho}{\rho} = \frac{\rho_H - \rho_0}{\rho}$, is $\leq 0.02$) and has very small $T$ dependence, as shown in the inset of Fig. 4.6. The other is a significant large negative MR, which increases very strongly as $T$ decreases. This negative MR dominates the small positive MR below a temperature $T' (=29 K$, defined as $MR=0$ at 7 T for the $a$-Gd$_{0.11}$C$_{0.89}$ sample). A similar $T'$ has also been found in Gd implanted $ta$-C ($ta$-C$_{1-x}$:Gd$_x$) samples [91].

$T'$ plays the role of $T^*$ previously discussed for $a$-Gd-Si [53], as the temperature below which Gd moments affect $\sigma_{dc}$, producing large negative MR [53]. $T^*$ could not be defined for these (or other) insulating samples. $T'$ is the temperature below which the negative MR due to carrier-moment interactions dominates the positive MR which is due to electron correlation effect in disordered electronic systems [46].

Figure 4.7 shows MR as a function of $H$ for the same sample. Large negative MR at 3 K, increasing with $H$, is visible. The inset expands the small MR region in order to show the positive MR as a function of the $H$ field. Three temperature regions can be identified. At high $T$ (>30 K), MR is positive up to 7 T. At moderate $T$ (5-22 K), MR is positive at low field and crosses over to negative MR at high field. The crossover field ($H_c$) decreases towards zero with decreasing $T$. Finally, at low $T$ (3 K), MR is strongly negative with a large $H$-dependence and does not saturate up to 7 T.

### 4.4.2 Magnetization

Figure 4.8 shows magnetization data for the $a$-Gd$_{0.093}$C$_{0.907}$:H$_{0.05}$ sample. This data is representative of all $a$-Gd$_x$C$_{1-x}$:(H$_y$) samples since they behave magnetically the same. A split was observed between susceptibility curves measured after field-cooled ($\chi_{FC}$) and after zero-field-cooled ($\chi_{ZFC}$), indicating spin-glass freezing, as previously seen and extensively discussed in $a$-Gd-Si alloys [48]. The spin-glass states are a result of competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions in disordered materials. Since the $f$ shell of Gd is very tightly bound to the nuclei, direct interaction between the Gd moments is very unlikely. A RKKY
Figure 4.7: (Color) MR vs $H$ on linear scale for $T = 3$, 5 and 30 K respectively. Inset shows MR data on expanded semilog scale near MR=0 for more temperatures. Small positive high-$T$ MR and large negative low-$T$ MR with a crossover between them at each temperature are visible.
Figure 4.8: (Color) Magnetization data for sputtered \( a\text{-Gd}_{0.093}\text{C}_{0.907}:\text{H}_{0.05} \) sample. dc susceptibility \( \chi=M/H \) for \( H=100 \) Oe measured after field cooling (\( \chi_{\text{FC}} \)) in 100 Oe and after zero field cooling (\( \chi_{\text{ZFC}} \)). ac susceptibility (\( \chi_{\text{AC}} \)) measured in 135 Hz 4 Oe. Curie-Weiss fit to data with \( p_{\text{eff}}=8.9 \mu_B \) and \( \theta=1.2 \) K, shown as a solid line. Inset (a) shows expanded scale of low-\( T \) data (\( T_f =3.8 \) K). Inset (b) shows \( M \) vs \( H \) at \( T=2 \) K for the same sample (line is a guide to the eye), compared to non-interacting Brillouin function.
(Ruderman-Kittel-Kasuya-Yosida) interaction was found in metallic Gd and GdSi$_2$ thus an indirect mediated RKKY-like exchange is likely the dominant interaction causing spin-glass freezing of our $a$-Gd-C(:H) alloys. A freezing temperature $T_f$ (roughly where $\chi_{ZFC}$ and $\chi_{FC}$ data split) was confirmed by ac susceptibility ($\chi_{AC}$) measurements, as shown in Fig. 4.8 inset (a). $T_f$ and $\chi$ increase with Gd concentration, both in the $a$-Gd-C samples and the $a$-Gd-C:H samples. We note that all our samples are insulators according to the vanishing zero temperature conductivity, and are highly disordered (amorphous), making the nature of an RKKY interaction different from the conventional crystalline metallic materials. The localization length of electrons near the $M$-$I$ transition is however significantly larger than the Gd-Gd spacing.

Above $T_f$, in the paramagnetic state, $\chi_{ZFC}$ and $\chi_{FC}$ overlap and both fit well to the Curie-Weiss (CW) law:

$$\chi_{ZFC,FC} = \frac{A}{T - \theta}.$$  \hspace{1cm} (4.2)

where $\theta$ is the CW temperature and the constant $A = n_{Gd}p^2\mu_B^2/3k_B$. The effective moment $p$ (8.0-9.0 $\mu_B$) extracted from $A$ is slightly higher than the value for a free Gd$^{3+}$ ion (7.9 $\mu_B$) presumably due to polarization of carriers. There is no Gd concentration dependence of $p$. $\theta$ is very close to 0 K ($|\theta| \lesssim 4$ K), slightly increasing with Gd doping. H incorporation does not have any significant effect on $p$ or $\theta$. This is not like the $a$-Gd$_x$Si$_{1-x}$ samples, where $p$ is suppressed and shows a nontrivial dependence on Gd concentration [48]. No superparamagnetic or clustered glass behavior or enhanced effective moment was found, further evidence that Gd is uniformly distributed in the $a$-C(:H) matrix and indirectly coupled via RKKY-like interaction.

Fig. 4.8 inset (b) shows the $M$ vs. $H$ for the same sample. The high $H$ magnetization is below but close to the non-interacting Brillouin function for free Gd$^{3+}$ ion, confirming the AFM interactions in the film. However, the magnetization response to $H$ is much larger than the $a$-Gd-Si samples, whose $M(H)$ curves are strongly suppressed below the Brillouin function due to much stronger AFM interactions [48].
4.5 Discussion

As shown in the inset of Fig. 4.5, $\sigma_{RT}$ increases then decreases, peaking at 11.0 and 13.5 at.% for $a$-Gd$_x$C$_{1-x}$ and $a$-Gd$_x$C$_{1-x}$H$_{0.2}$ respectively. The non-monotonic $x$ dependence of $\sigma_{RT}$ indicates that, in addition to electrically doping $a$-C(:H), Gd has other effects on the film properties when the doping level is high, which cause the overall $\sigma_{dc}$ to decrease. As a result, a concentration-tuned $M$-$I$ transition is not achieved for the $a$-Gd$_x$C$_{1-x}$(:H$_y$) samples. In $a$-Gd-Si alloys, $\sigma_{dc}$ decreased above 25 at. % Gd, due to formation of nano-crystalline clusters observable in the HR-XTEM micrographs [26]. Here, however, no crystalline clusters are observed in HR-XTEM micrographs (up to 22 at.% and 15.6 at.% for $a$-Gd-C and for $a$-Gd-C:H respectively).

Another possible explanation of the $\sigma_{dc}$ drop is reduced electronic density due to low atomic number density ($n$) of the amorphous film. $a$-C has many possible morphologies depending on the $sp^2/sp^3$ ratio and arrangement. Gd dopants could introduce large local defects (e.g. voids) and lead to less dense $a$-C(:H) matrix, which should be reflected in a decrease of total number density ($n_{total}$) of the film. We however do not observe any significant drop of $n_{total}$ near the $\sigma_{dc}$ maximum. If we let six carbon atom replace one Gd atom in these doped films, we can estimate the effective mass density ($\rho$) of the $a$-C(:H) matrix, which is between 1.9-2.6 g/cm$^3$, consistent with good quality sputtered $a$-C(:H) films in the literature [54], and ruling out porous phase of $a$-C(:H), which has very low electronic density thus very low $\sigma_{dc}$.

We argue that the explanation for the nonmonotonic behavior of $\sigma_{dc}$ can be deduced from the Raman spectra, which show an unambiguous change in the $sp^2$ arrangement with Gd doping, correlated with the concentration dependence of $\sigma_{RT}$ as shown in Figure 4.9. The $I_D/I_G$ ratio first increases and then decreases, peaking at the same Gd concentration where $\sigma_{RT}$ reaches its maximum for both $a$-Gd-C and $a$-Gd-C:H. Samples with the highest $\sigma_{dc}$ have the largest $I_D/I_G$ ratio, indicating more disordered graphitic ring sites. These sites increase the $\sigma_{dc}$ of the $a$-C(:H) matrix. The overall $\sigma_{dc}$ for the high Gd concentration samples can be treated as a sum of $\sigma$ of the $a$-C(:H) matrix and of the Gd doping sites, as in a
Figure 4.9: (Color) $\sigma_{RT}$ and $I_D/I_G$ as function of Gd concentration for (a) $a$-Gd$_x$C$_{1-x}$:H$_{0.20}$ (b) $a$-Gd$_x$C$_{1-x}$.
two-channel conductivity model. Before reaching the $\sigma_{dc}$ maximum, the increasing Gd at.% and graphitic ring sites both contribute to the increasing $\sigma_{dc}$. However, the graphitic ring sites start to decrease after reaching the threshold doping and the matrix becomes less conducting. This compensates the doping effect of Gd and is responsible for the decreasing overall $\sigma_{dc}$.

Turning now to the magneto-transport properties, there are few theoretical models to describe the large negative MR in magnetically-doped disordered electronic systems. The bound magnetic polaron (BMP) model was used to explain the negative MR in doped crystalline semiconductor systems such as Cd$_{1-x}$Mn$_x$Se [92] and Gd$_{3-x}\nu_x$S$_4$ [4]. Our system however, has a much higher ratio of carriers to magnetic dopant sites compared to the above systems (of order 1:1 vs. 1:10$^4$). Thus, BMP is not a relevant model. Instead we turn to an Anderson localization type model to explain the negative MR. The interaction between carriers and the randomly oriented Gd moments provides additional magnetic disorder to the structural disorder thus increasing the localization of the hopping carriers. Applying $H$ reduces the magnetic disorder and increases the hopping conductance. This picture can qualitatively explain the large negative MR and emphasizes a single tunable parameter, namely the degree of disorder in both structure and magnetization, in these systems.

4.6 Conclusion

We have successfully prepared uniformly doped $a$-Gd$_x$C$_{1-x}$(:H$_y$) samples with $x$ up to 22 at.% and with variable amounts of H. For all samples, the magnetic ground state is a spin-glass with $T_f$ between 2-6 K, scaling with $x$. Above $T_f$, the magnetic susceptibility $\chi$ follows a Curie-Weiss law with $\theta \sim 0$ K and $p_{eff} \sim 8.0$ - 9.0 $\mu_B$, very close to the expected 7.9 $\mu_B$ for Gd$^{3+}$ and independent of $x$. $\sigma_{dc}(T)$ initially increases with $x$, but decreases above 11 at.% (13.5 at.% for the hydrogenated samples) and is strongly correlated to the amount of graphitic ring sites in films. Gd incorporation favors formation of graphitic $sp^2$ sites, while H incorporation opens up the graphitic rings, stabilizes $sp^2$ chains and makes the $a$-C(:H) matrix more “diamondlike” hence lower $\sigma_{dc}(T)$. Raman $I_D/I_G$ ratio after Gd dop-
ing is larger than most pure $a$-C(:H) reported in the literature, suggesting that further modeling of the local bonding structure in this Gd-doped $a$-C material would be appropriate. The large low-$T$, high-$H$ negative MR provides strong evidence of large interactions between the Gd moments and the charge carriers. A systematic study of the magnitude and onset temperature of the large negative MR by manipulating carbon matrix morphology towards more diamondlike (more $sp^3$ fraction, higher band gap) could shed light on the underlying physics and is currently under active investigation.

4.7 Acknowledgement

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5

$ta-C_{1-x}:Gd_x$ films

5.1 Introduction

Gd-implanted tetrahedral amorphous carbon ($ta$-$C$) was prepared by Gd ion implantation into $ta$-$C$ ($ta$-$C_{1-x}$:Gd$_x$, $x=0.022$~$0.20$) grown by mass-selected ion-beam deposition (MS-IBD). As we have discussed in Chapter 3, Gd is found to be always in a trivalent state, with a half-filled $f$ electron shell ($J=S=7/2$), which provides three electron carriers and a large local moment. Gd-doped $a$-$Si$ ($a$-Gd$_x$Si$_{1-x}$) films have shown important carrier-moment interactions, indicated by their spin-glass ground state, unsaturated magnetization at high field and enormous negative MR ($10^4$ at 1 K, in a 60 kOe field). However, when doping Gd into $a$-$Ge$ ($a$-Gd$_x$Ge$_{1-x}$), all interactions become smaller [33]. Therefore, it has been speculated that in $sp^3$-rich carbon with a wide band gap, the MR will increase. Since $a$-$C$ is typically a mixture of $sp^2$ and $sp^3$ bonds, the band gap depends on the $sp^2/sp^3$ ratio. As shown in Chapter 4, sputtered $a$-$C$ is mostly $sp^2$-bonded, with a small band gap. Nevertheless, large negative MR is found at low temperatures, comparable to that of the $a$-Gd$_x$Si$_{1-x}$.

MS-IBD is quite a different deposition method than sputtering. The kinetic energy of the deposited ions can be controlled by an electrical field up to hundreds of eV. This is used to prepare the metastable $ta$-$C$ films with high $sp^3$ fractions up to 80% and provides a new type of amorphous semiconductor matrix for the study of the magnetic ion incorporation. The implantation method used for Gd
incorporation is speculated to affect the ta-C film structure. Understanding the structure of the resulting ta-C$_{1-x}$:Gd$_x$ films and their physical properties, such as dc transport, magnetization and magneto-transport properties, is the main focus of this work.

5.2 Experimental Methods

$ta$-C with high $sp^3$ fraction is a metastable phase at ambient conditions. The $ta$-C films for this Gd implantation study were prepared with a very energetic physical deposition method, mass-selected ion-beam deposition (MS-IBD), onto 400 nm insulating SiN$_x$-coated Si substrates for magnetic and magneto-transport measurements. The kinetic energy of deposited carbon was $\sim$100 eV in order to maximize the $sp^3$ bonding fraction [54]. The $ta$-C films are isotopically pure and exhibit $\sim$80% $sp^3$ bonds with a high mass density of 2.9 g/cm$^3$, showing diamond-like properties [93]. Deposition was done at pressure below $3 \times 10^{-8}$ Torr at room temperature. The thicknesses of $ta$-C films are between 40-60 nm. Then $ta$-C samples were implanted by $^{155}$Gd ions at an ion energy of 50 keV and a varying ion influence in order to change the Gd doping concentration. Double-energy (30 and 50 keV) implantations were also carried out in order to achieve a more uniform Gd doping profile. The implantation temperature ($T_i$) was at room temperature. A set of Xe-implanted $ta$-C films ($ta$-C$_{1-x}$:Xe$_x$) prepared under the same implantation conditions were used as control samples. The resulting film compositions were calculated by the transport of ions in matter (TRIM) simulation and verified by RBS measurements. Generally agreement between these two methods were achieved. Raman spectra were obtained using a 488-nm laser and a SPEX 1877 0.6 m Triple Spectrometer. dc transport was measured using a standard four-point-probe method with conducting silver paint strips as electrical contacts. The sample magnetization (both $T$ and $H$ dependence) as well as magneto-electronic properties were measured in a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Annealing studies were performed in a rapid thermal annealer. A typical temperature profile for annealing consists of three stages: a two-minute temperature rise, an one-minute temperature soak and an
exponential temperature decay back to room temperature. During the annealing process, samples were kept in continuously flowing forming gas (5% H$_2$ in N$_2$) to avoid oxidation. All measurements and annealing treatments were also performed on the $ta$-$C_{1-x}$:Xe$_x$ control samples. More experimental details were presented in Chapter 2. A summary of sample information on $ta$-$C_{1-x}$:Gd$_x$ films is presented in Table 5.1.

5.3 Experimental Results

5.3.1 Materials Characterization

RBS data for selective samples were analyzed by the RUMP analysis package. The results show that there is an undoped surface layer (generally found in implanted samples). The thickness of this top layer is $\sim$10 nm for low-dose samples, and decreases to $\sim$5 nm for the highest dose due to the sputtering effect. These results agree with the TRIM simulation. We define the Gd concentration $x$ from the RBS RUMP analysis, which is generally different from the peak concentration (note that the RBS composition uncertainty is close to 0.01). This difference is because the RUMP simulation assumes a homogeneous distribution of dopants within a depth profile instead of a Gaussian distribution. As shown in Fig. 5.1, for this particular single-energy implanted sample ($ta$-$C_{0.96}$:Gd$_{0.04}$), the “RBS thickness” is 8 nm while the full width of the Gaussian distribution is 19 nm. Double-energy implantation greatly reduces these discrepancies. For consistency, the thicknesses used for conductivity calculation are $\sim$19 nm and $\sim$20 nm for the single-energy and the double-energy implanted samples, respectively, based on the full width of the ion distribution from the TRIM simulation.

Raman spectroscopy was used to obtain carbon bonding information of the $ta$-C films before and after Gd/Xe implantation, as well as after thermal annealing. As discussed in Chapter 2, with 488 nm laser excitation, there are two major Raman active modes corresponding to the breathing mode of disordered graphitic 6-member rings (the $D$ peak, $\sim$1350 cm$^{-1}$) and the stretching mode of C-C pairs (the $G$ peak, $\sim$1580 cm$^{-1}$), respectively. Using the integrated peak intensity ratio
Figure 5.1: (Color) (a) TRIM simulation; (b) RBS data and RUMP simulation for a single-energy implanted sample. The best fit gives the layered structure after implantation: C(10 nm)/ta-C_{0.94}:Gd_{0.04} (8 nm)/ta-C (35 nm).

\( \frac{I_D}{I_G} \); both peaks are fitted to a Gaussian function unless otherwise mentioned), according to the three-stage model for a-C’s Raman spectroscopy [59] as mentioned in Chapter 4, one can estimate the \( sp^2/sp^3 \) ratio of the films.

The Raman spectra of undoped as-grown ta-C films with high \( sp^3 \) fraction show a predominant G peak due to the lack of graphitic ring sites, thus very small \( I_D/I_G \) ratio. Annealing up to 550 °C in a reducing environment does not change the Raman spectra of the pure ta-C films very much, consistent with results in the literature [93]. The strong \( sp^3 \) covalent bonds, once formed, are very stable under thermal treatments, since the energy barrier for converting \( sp^3 \) to \( sp^2 \) is large (oxygen can act as a catalyst to lower this barrier, thus annealing in vacuum or a reducing environment is essential). Diamond can be annealed in vacuum at a temperature as high as 1800 K (\( \sim 155 \) meV) without graphitization (see chapter 13.3 of Ref. 94). There is, however, a small increase of the \( I_D/I_G \) for annealed ta-C films. This is presumably due to the graphitization of the \(<20\% \ sp^2\)-bonded carbon chains in as-grown ta-C films.

Prior to understanding the properties of ta-C\(_{1-x}:\)Gd\(_x\), it is informative to study the radiation-induced matrix changes. Xe and Gd ions have almost the identical radii and very similar atomic masses, therefore, the radiation damage of ta-C ma-
trix due to nuclear collisions (i.e., close encounter Coulombic interactions which displace the matrix atoms) should be similar under the same implantation conditions (the implantation dose, temperature and kinetic energy etc). The differences are, first, the Xe atom has a stable closed-shell electron structure which does not contribute any electrical or magnetic signal (it will contribute a Langevin diamagnetic response, but this is very small). Secondly, Xe atom is chemically inert and does not form chemical bonds. \(ta\text{-}C_{1-x}\text{:Xe}_x\) films thus provide us with the information on any radiation-damage-related effects, if any, in the \(ta\text{-}C_{1-x}\text{:Gd}_x\) films. Any difference between the \(ta\text{-}C_{1-x}\text{:Gd}_x\) and \(ta\text{-}C_{1-x}\text{:Xe}_x\) films comes from the incorporation of Gd ions, either electrically or magnetically, as well as any bonding structure changes of the \(ta\text{-}C\) matrix due to the Gd.

Figure 5.2 and 5.3 shows the normalized line shapes of the Raman spectra of all \(ta\text{-}C_{1-x}\text{:Xe}_x\) and \(ta\text{-}C_{1-x}\text{:Gd}_x\) films, respectively. Fig. 5.2 shows that the change of the \(ta\text{-}C\) Raman spectra after Xe implantation is small. Quantitative analysis shown in Fig. 5.4 presents \(I_D/I_G\) values and the total Raman intensity \((I_D+I_G)\) as a function of Xe concentration. The \(I_D/I_G\) ratio is increased for \(x\) above 0.04 but the values are small \((\sim 2.3)\) and constant, up to \(x=0.20\). The total Raman intensity increases monotonically after an initial drop from undoped \(ta\text{-}C\) film.

These results of \(ta\text{-}C_{1-x}\text{:Xe}_x\) samples indicate that there are changes of the matrix due to the energetic implantation process, but very few \(sp^3\) bonds have been converted to \(sp^2\) bonds. These results are consistent with the study of radiation-induced transformation of diamond [95]. \(T_i\) is at room temperature, considering not enough to have the dynamic annealing effect which can in-situ heal the implantation damage and keep the \(sp^3\) phase stable during the implantation. The critical temperature to have dynamic annealing occur was found to be at least 815 K [95]. This explains the small increase of \(I_D/I_G\). On the other hand, \(T_i\) is also too low to have the radiation-induced defects graphitize into highly conducting \(sp^2\) rings sites, so the \(I_D/I_G\) does not increase much.

Figure 5.3 shows the Raman spectra of \(ta\text{-}C_{1-x}\text{:Gd}_x\) normalized to peak height in order to show the effect of Gd implantation on line shape. In contrast to the \(ta\text{-}C_{1-x}\text{:Xe}_x\) samples, there are dramatic changes of the Raman spectra after the Gd implantation. Fig. 5.5 shows \(I_D/I_G\) ratio and \(I_D+I_G\) as a function of Gd
Figure 5.2: (Color) Raman spectra of $ta$-$C_{1-x}$:$Xe_x$ films. Solid lines are the single-energy implanted samples. The dotted line is an annealed sample for comparison. Dash dotted lines are the double-energy implanted samples.
Figure 5.3: (Color) (a) Raman spectra of ta-C$_{1-x}$:Gd$_x$ films with single-energy implantation. (b) Raman spectra of ta-C$_{1-x}$:Gd$_x$ films with double-energy implantation. The two dashed lines are samples with high-Xe doses for comparison. Note the apparent difference between the high dose ta-C$_{1-x}$:Gd$_x$ and ta-C$_{1-x}$:Xe$_x$ Raman spectra.
concentration, showing some noticeable differences from the $ta$-$C_{1-x}$:$Xe_x$ Raman spectra. The $I_D/I_G$ first increases for the $x=0.04$ sample, but then decreases for the $x=0.07$ sample. For $x=0.20$, there is a dramatic change in the Raman line shape (as shown in Fig. 5.3) and a strong decrease of the Raman intensity, which leads to poorly defined $D$ and $G$ peaks. Thus the $I_D/I_G$ ratio is not meaningful (thus connected by a dashed line in Fig. 5.5). The spectrum for the high Gd dose ($x=0.20$) as shown in Fig. 5.3 does not resemble any Raman spectra documented for $a$-$C$ in the literature.

Figure 5.6 shows the raw Raman spectra for the $ta$-$C_{1-x}$:$Gd_x$ films to emphasize the large but different effects of Gd implantation on the $ta$-$C$ matrix compared with Xe-implanted samples. As we mentioned, the Raman intensity of the $ta$-$C_{1-x}$:$Xe_x$ films slightly increases with Xe dose. However, as shown in Fig. 5.6, the Raman intensity of the $ta$-$C_{1-x}$:$Gd_x$ films decrease monotonically and dramatically with the Gd dose. The inset shows $I_D+I_G$ for both the Gd and the Xe-implanted films as a function of dose. For $x=0.04$, both have similar Raman intensities. For
Figure 5.5: (Color) The $I_D/I_G$ ratio and peak intensity ($I_D+I_G$) vs Gd $x$ (decreases with the Gd dose) for the $ta$-$C_{1-x}$:Gd$_x$ films. At $x=0.2$, peaks are not well defined.

$x \geq 0.07$, the intensity for $ta$-$C_{1-x}$:Xe$_x$ increases slightly with $x$, while the intensity for $ta$-$C_{1-x}$:Gd$_x$ decreases with $x$. The opposite trend in $ta$-$C_{1-x}$:Gd$_x$ suggests that besides radiation damage to the matrix (as the Xe does), Gd produces additional effects on the $ta$-$C$ matrix. The decrease of the overall intensity at these two $a$-$C$ active Raman modes may be due to a ‘softening’ of the $a$-$C$ lattice by forming possible new bonds which do not contribute to these two modes.

After post-implantation rapid thermal annealing (RTA) treatment, $I_D/I_G$ increases for both Xe-implanted and Gd-implanted films. The amplitude of increase scales with the implantation dose. This can be understood by graphitization of the radiation-induced damage centers, which include large amount of vacancies, interstitials, dangling bonds or defect clusters. Due to the low $T_i$, although there is some initial graphitization, most of the damage centers are “frozen” and bond rearrangement is unlikely. Fig. 5.4 shows that $I_D/I_G$ does not increase with $x$ for the as-implanted $ta$-$C_{1-x}$:Xe$_x$ samples. After annealing at sufficiently high temperature, vacancies and interstitials become mobile, and local bond rearrangement
Figure 5.6: (Color) The raw Raman peaks for single-energy implanted \( ta-C_{1-x}:Gd_x \) samples. Inset shows peak intensity \( (I_D+I_G) \) vs \( x \) for both \( ta-C_{1-x}:Xe_x \) and \( ta-C_{1-x}:Gd_x \) films.
is possible. This results in the formation of stable $sp^2$-bonded graphitic sites which gives rise to a more intense Raman $D$ peak and much larger $I_D/I_G$ ratio ($\sim 8$) after annealing.

### 5.3.2 Magnetization

![Graph showing ZFC and FC susceptibility versus temperature](image)

Figure 5.7: (Color) ZFC and FC $\chi$ vs $T$ for the double energy implanted $ta$-$C_{0.824}$-$Gd_{0.176}$ sample near the SG freezing. Inset: expanded temperature range of $\chi(T)$, which follows the CW law above estimated $T_f$.

For $x \leq 0.07$, sample magnetization shows a pure paramagnetic behavior, where magnetic susceptibility data $\chi(T)$ follow the Curie-Weiss behavior very well. For $x = 0.088$, $\chi(T)$ starts to show slight deviation from the CW behavior at low $T$. The deviation is obvious in the single-energy implanted $ta$-$C_{0.80}$-$Gd_{0.20}$ sample; $\chi(T)$ flattens out for $T$ below 6 K. These data indicate magnetic interactions develop with implantation doses. A clear spin-glass (SG) freezing, indicated by a split between ZFC and FC $\chi(T)$ data as shown in Fig. 5.7, was observed in the double-energy-implanted $ta$-$C_{0.824}$-$Gd_{0.176}$ sample, which has the highest Gd dose of $4.6 \times 10^{16}$ Gd/cm$^2$. The estimated $T_f$ from the splitting between the ZFC and FC data is 5 K. For all $ta$-$C_{1-x}$-$Gd_x$ of the paramagnetic state, the effective moments
$p_{\text{eff}}$ obtained from the CW fitting are between 8-10 $\mu_B$ (shown in Table 5.1), while for a free Gd$^{3+}$ ion $p_{\text{eff}}=7.9$ $\mu_B$. This slightly larger $p_{\text{eff}}$ is presumably due to polarization of $s$ electrons by the $s$-$f$ exchange interaction.

![Graph of $M(H)$ vs $H$ for various temperatures](image)

Figure 5.8: (Color) $M$ vs $H$ data for the double-energy-implanted $ta$-$C_{0.824}:Gd_{0.176}$ sample at various temperatures. Inset: hysteresis loop below $T_f$ (2 K). $M(H)$ at $T=2$ K for a cosputtered $a$-$Gd_{0.13}Si_{0.87}$ film is also plotted for comparison. The Brillouin function for $j=7/2$ at 2 K is shown as a solid line.

Figure 5.8 shows the magnetic field dependence $M(H)$ of the $x=0.176$ sample at various temperatures. For the lowest measured temperature ($T=2$ K), $M(H)$ is well below the Brillouin function for free $J=S=7/2$ ions and shows a small hysteresis loop, which is consistent with the SG behavior seen in the $\chi(T)$ data. Compared with the $a$-$Gd_xSi_{1-x}$ films (discussed in Chapter 3), the AFM interactions are weaker in $ta$-$C_{1-x}:Gd_x$. $M(H)$ curve for a cosputtered $a$-$Gd_{0.13}Si_{0.87}$
sample is also shown in Fig. 5.8 for direct comparison. The moment is suppressed much lower below the Brillouin function for the $a\text{-Gd}_{0.13}\text{Si}_{0.87}$ sample, indicating stronger AFM interactions. For the $ta\text{-C}_{1-x}\text{:Gd}_x$ films, the saturation moment at high fields and the low-field susceptibility are relatively close to the Brillouin function. These results are similar to what was found in cosputtered $a\text{-Gd}_x\text{C}_{1-x}$ films.

### 5.3.3 dc Transport and Magnetoresistance

Figure 5.9 shows dc conductivity vs $T$ [$\sigma_{dc}(T)$] for all $ta\text{-C}_{1-x}\text{:Gd}_x$ films. $\sigma_{dc}$ is greatly increased after Gd doping in comparison with the low $\sigma_{dc}(295\ \text{K})\sim10^{-9}\ \Omega^{-1}\text{cm}^{-1}$ of undoped $ta\text{-C}$ films. The Gd doping effect is confirmed by measuring $ta\text{-C}_{1-x}\text{:Xe}_x$ control samples. Although the implantation doses exceed the critical dose ($D_c\sim3\times10^{-14}\ \text{atoms/cm}^{-2}$) to form a percolation path between the damaged centers [95], the conductivity of $ta\text{-C}_{1-x}\text{:Xe}_x$ is 2 orders of magnitude lower than $ta\text{-C}_{1-x}\text{:Gd}_x$ at room temperature (much more at low $T$). The film conductivity clearly not only depends on the connectivity of these centers, but also on local carrier density. The radiation-induced density of states at the Fermi level in diamond is very low [$N(\epsilon_F)\sim10^{19}\ \text{states/eV\cdotcm}^3$] [95], thus the contribution to conductivity is small. We conclude that the major contribution to $\sigma_{dc}$ for $ta\text{-C}_{1-x}\text{:Gd}_x$ is not due to the radiation-induced damage of the $ta\text{-C}$ matrix. Instead, the additional carriers comes from Gd doping, which likely donates $3e^-$ per Gd$^{3+}$ ion. The large room temperature $\sigma_{dc}$ indicate a large number of carriers near the Fermi surface, subject to strong localization effects in these highly disordered materials. As $T$ drops, all $ta\text{-C}_{1-x}\text{:Gd}_x$ samples are found to be on the insulating side of the $M$-$I$ transition, since $\sigma_{dc}(T\rightarrow0\ \text{K})\rightarrow0$ even for $x=0.20$; much higher than the critical concentration found in other Gd-doped semiconductors, which is $\sim0.14$. Figure 5.9 inset shows that $\sigma_{dc}$ does not increase monotonically with $x$; instead, $\sigma_{RT}$ decreases for $x>0.09$. This nonmonotonic concentration dependence of $\sigma_{dc}$ is similar to sputtered $a\text{-Gd}_x\text{C}_{1-x}$ films. Unlike sputtered $a\text{-Gd}_x\text{C}_{1-x}$ films, no correlation between the $I_D/I_G$ and the $\sigma_{RT}$ is found.

Despite the quite different film growth processes of preparing Gd-doped $a\text{-C}$
Figure 5.9: $\sigma_{dc}(T)$ for both single-energy implanted (blue dashed curves) and double-energy implanted (red solid curves) samples. Inset: room temperature conductivity $\sigma_{RT}$ as a function of Gd $x$. 

Note: $\sigma_{RT}$ (at-C) $\sim 10^{-9}$ (Ω cm)$^{-1}$
(magnetron cosputtering [96] or by IBD followed by ion-implantation), all Gd-doped \( a-C \) samples have similar type of magneto-transport. The temperature dependence of the MR shows a high-\( T \) small positive MR with almost no \( T \) dependence and a low-\( T \) enormous negative MR which is strongly \( T \) dependent. The magnitudes of the low-\( T \) MR are of the same order of magnitude for sputtered \( a-Gd_xSi_{1-x} \) and \( a-Gd_xC_{1-x} \) (MR\( \sim 10^3 \) at 3 K, 60 kOe), and much larger than \( a-Gd_xGe_{1-x} \) films. On the other hand, \( a-Gd_xSi_{1-x} \) and \( a-Gd_xGe_{1-x} \) both have negative MR up to 100 K and do not switch sign to positive MR. For Si and Ge matrices, a characteristic temperature \( T^* \) is defined for samples on the metallic side by comparison to non-magnetic doping analogues: \( a-Y_xSi_{1-x} \) or \( a-Y_xGe_{1-x} \) [33,53] (discussed in Chapter 3). For insulating samples including \( ta-C_{1-x}:Gd_x \) samples, \( T^* \) cannot be defined. Instead, we define \( T' \) as in Chapter 4, as the temperature at which MR switches from positive to negative in a 70 kOe field. This crossover temperature \( T' \) is not as rigorously defined as \( T^* \) which is measured in zero field thus a ground-state characteristic temperature. However, \( T' \) plays a similar role as \( T^* \), providing the \( T \) scale below which Gd carrier-moment interactions cause negative MR, which dominates the small positive MR found in non-magnetic disordered electron systems due to electron correlation effects.

5.4 Discussion

Raman line shapes and \( I_D/I_G \) values indicate that the matrix of \( ta-C_{1-x}:Gd_x \) films is less graphitic than cosputtered \( a-Gd_xC_{1-x} \) films. For \( a-Gd_xC_{1-x} \) films, the \( I_D/I_G \) ratio can be as high as 12 and the Raman spectra show a distinct \( D \) peak corresponding to the \( sp^2 \)-bonded graphitic rings with increasing Gd \( x \). \( \sigma_{RT} \) was found to be correlated to the graphitic site fraction in the sputtered \( a-C \) matrix [96]. For Gd \( x \) above a threshold doping \( (x_{th} \sim 0.11 \) for \( a-Gd_xC_{1-x} \)), \( \sigma_{dc} \) at room temperature decreases with \( I_D/I_G \) even with increasing Gd \( x \). No such correlation between \( I_D/I_G \) and \( \sigma_{dc} \) was found in \( ta-C_{1-x}:Gd_x \). We suggest this is because \( ta-C \) is quite a different matrix from the sputtered \( a-C \), and the incorporation of Gd by implantation also affect the carbon matrix differently from cosputtering. The decrease of \( \sigma_{dc} \) at high Gd dose is related to the dramatic change
of Raman line shape and the decrease of Raman intensity. No reliable $I_D/I_G$ ratio can be obtained for $x>0.09$ in contrast to sputtered $a$-Gd$_x$C$_{1-x}$ films. For $x \leq 0.088$, the radiation-induced damage centers in ta-C matrix are much less conducting and are not converted into graphitic sites without RTA treatment, so $\sigma_{dc}$ only increases with $x$ and shows no dependence on $I_D/I_G$ ratio and matrix graphitization. More materials characterization, such as HR-XTEM, could potentially shed more light on this non-monotonic dependence of $\sigma_{dc}$ on $x$.

RTA treatment greatly increases $\sigma_{dc}$ by orders of magnitude. This is due to the bond rearrangement within damage centers leading to a much more conducting graphitic matrix, indicating by the Raman spectra. Even though for the as-implanted samples, the Raman spectra do not show a significant change, the low-$T$ energetic implantation process has already destabilized the $sp^3$ metastable bonds, and the damage centers serve as precursors for $sp^2$ nucleation. Films become metallic due to these metallic graphitic centers in the matrix. MR becomes smaller due to the large increase of $\sigma_{dc}$, although $\Delta \sigma_{dc}$ increases. $T'$ decreases with the annealing temperature [91].

Figure 5.10 shows the low-$T$ resistance as $\log R$ vs $T^{-\alpha}$. The exponent $\alpha$ can be 1/4, 1/2 or 1, corresponding to different transport mechanisms: 3D Mott VRH, ES VRH or a single activation energy hopping, respectively. The best fit is found for $\alpha=1/2$, as for other Gd-doped amorphous semiconductors. After applying a magnetic field, the range of $\sigma_{dc}(T)$ that fits to $T^{-1/2}$ is increased to higher temperature.

The enormous low-$T$ negative MR for ta-C$_{1-x}$:Gd$_x$ is the high light of this material, as in $a$-Gd$_x$C$_{1-x}$ films. Figure 5.11 shows $T'$ as a function of Gd $x$ for all Gd-doped carbon materials. A linear increase of $T'$ with $x$ is found, in contrast to the decreasing $T^*$ with metallicity (either by increasing doping $x$ or by changing the matrix from $a$-Si to $a$-Ge). However, since $\sigma_{dc}$ does not increase monotonically with $x$, given the different way we define $T'$, direct comparison of the $x$ dependence of $T'$ and $T^*$ needs more careful analysis.
Figure 5.10: (Color) log$R(T)$ as a function of $T^{-\alpha}$ ($\alpha=1/4$, 1/2 and 1, respectively). $\alpha=1/2$ fits better for a wider $T$ range at low $T$ and for in-field resistance. The open (blue) circles are data for $ta$-$C_{1-x}$:$Xe_x$ films.

Figure 5.11: (Color) $T'$ as a function of Gd doping $x$ for different $a$-C matrices, including sputtered $a$-$C$(:H) films, IBD $ta$-$C$ films, and microcrystalline diamond (MCD) and nanocrystalline diamond (NCD) films.
5.5 Conclusion

In summary, ta-C thin films provide a new type of a-C matrix to study the moment-carrier interactions in its magnetically doped form. Radiation-induced damage alone cannot account for the largely increased conductivity, and the electrical doping effect of Gd is obvious. Only after the thermal annealing treatment, the radiation-induced damage centers are converted into $sp^2$-bonded graphitic sites, providing a metallic matrix. The as-implanted samples are insulators. Gd ions act as non-interacting large local $f$ moments in the paramagnetic states with no sign of clustering. There is strong evidence of moment-carrier interactions. $p_{\text{eff}}$ of Gd is higher than the 7.9 $\mu_B$ in the paramagnetic state likely due to $s$ electron polarization. SG freezing is observed for high dose samples due to carrier-mediated RKKY-like interactions, as in other Gd-doped amorphous semiconductors. An enormous negative MR is found in all $ta$-$C_{1-x}$:Gd$_x$ films. This negative MR is attributed to a magnetic disorder-induced carrier localization. In this model, applying a magnetic field aligns the Gd moments, which increases the VRH conductivity. A crossover temperature $T'$ increases with Gd concentration.
Table 5.1: $ta$-$C_{1-x}:Gd_x$ Sample Information.

<table>
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<tr>
<th>$x$</th>
<th>ta-C thickness (nm)</th>
<th>$^{155}$Gd$^{3+}$ fluence ($\times 10^{15}$ atoms/cm$^2$)</th>
<th>Gd energy (keV)</th>
<th>$p_{\text{eff}}^2$ (µB)</th>
<th>$\sigma_{\text{IR}}$ ($\Omega$-cm)$^{-1}$</th>
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<td>50</td>
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<tr>
<td>0.070</td>
<td>42</td>
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<td>50</td>
<td>9.35</td>
<td>230.6</td>
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<tr>
<td>0.200</td>
<td>42</td>
<td>40</td>
<td>50</td>
<td>8.80</td>
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<tr>
<td>0.022</td>
<td>43</td>
<td>2.5+3.25</td>
<td>30+50</td>
<td>9.02</td>
<td>39.7</td>
</tr>
<tr>
<td>0.088</td>
<td>61</td>
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<td>30+50</td>
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<td>0.176</td>
<td>43</td>
<td>20+26</td>
<td>30+50</td>
<td>8.12</td>
<td>161.0</td>
</tr>
</tbody>
</table>

$^1$Based on RUMP simulation of RBS data

$^2$p$_{\text{eff}}$ per Mn obtained from CW constant $A = n_{\text{Mn}}p_{\text{eff}}^2\mu_B^2/3k_B$
We have prepared samples of Mn-doped amorphous Si ($a$-Mn$_x$Si$_{1-x}$) using $e$-beam coevaporation. Transport data indicate that Mn acts as an electrical dopant. Unlike the large negative MR observed in Gd-doped samples, $a$-Mn$_x$Si$_{1-x}$ has a very small positive MR. This is attributed to an absence of a Mn local moment in the amorphous silicon matrix. The magnetic susceptibility obeys the Curie-Weiss law for a wide range of $x$ ($5 \times 10^{-3}$ up to 0.175) but with extremely small moment. Both magnetization and X-ray absorption data suggest that this is because only a small percentage of Mn (interstitial Mn$^{2+}$ states with $J=S=5/2$) contribute to the magnetization. Thus, the magnetic moments are quenched for the majority of Mn atoms, contrary to the general belief of the existence of a localized moment at Mn doping sites in silicon. This quenching of Mn moments is attributed to the formation of an itinerant but Anderson-localized impurity band, forming at $x$ as low as $5 \times 10^{-3}$.
6.1 Introduction

Mn has been widely used as a magnetic dopant in dilute magnetic semiconductors (DMSs), which have potential applications as spintronic materials. While many Mn-doped systems are antiferromagnetic (AFM), ferromagnetism was found in Mn-doped III-V semiconductors, such as (Ga, Mn)As, first reported by Ohno [7]. Both mean-field theory (the Zener model) [12] and first-principles calculations [14, 97] have predicted that room temperature ferromagnetism is possible in Mn-doped group-IV semiconductors. Interactions and mixing of the Mn \(d\) electrons in different host environments will lead to different charge and spin states, which greatly affect the magnetic ordering [98]. There is a strong recent focus on research into Mn-doped crystalline Ge (c-Ge) and Si (c-Si) [13, 15–19]. Mn-doped c-Si, in particular, is of much interest due to its compatibility with Si-based semiconductor technology. However, the solubility of Mn in crystalline group-IV semiconductors is extremely low. Therefore, to stabilize Mn doping above the solid solubility limit, one must utilize highly non-equilibrium doping techniques such as low temperature molecular beam epitaxy (MBE) [99] or ion-implantation [13, 98]. Recent studies on Mn-implanted crystalline Si (c-Si\(_{1-x}:\text{Mn}_x\)) thin films prepared by the latter technique have achieved Mn doping levels of a few atomic percent \((x \leq 0.05)\) [15, 16].

Ferromagnetism [Curie temperature \((T_C)\) up to 116 K] was observed in Mn-doped c-Ge (c-Mn\(_x\)Ge\(_{1-x}\)) and a long-range ferromagnetic (FM) interaction dominating over a short-range Mn-Mn AFM interaction was proposed as the origin of the ferromagnetism [13]. Determining whether the ferromagnetism in Mn-doped c-Ge and c-Si is intrinsic or not in origin, is however, very challenging due to thermodynamically favorable FM second phases or possible nano-structures, which are hard to detect by conventional structural characterization tools. Recent studies, including sub-micron scanning photoelectron microscopy (SPEM), high-resolution transmission electron microscopy (HR-TEM) and synchrotron x-ray diffraction, have shown chemical inhomogeneity in c-Ge\(_{1-x}:\text{Mn}_x\) [18] and the existence of MnSi\(_{1.7}\) nano-crystallites in c-Si\(_{1-x}:\text{Mn}_x\) [19]. The ferromagnetism in these systems was attributed to a Mn-rich Ge phase [18] and MnSi\(_{1.7}\) nano-crystallites [19].
in the former and latter systems, respectively.

The intrinsic magnetic states of Mn in Si as a function of Mn concentration can be addressed by preparing homogeneous Mn-doped amorphous Si (a-Si). High quality e-beam-evaporated a-Si consisting of a continuous random network (CRN) [25] of tetrahedrally-bonded Si atoms, possesses a local chemical environment similar to that of crystalline Si (c-Si). Moreover, lower growth temperatures and the more forgiving nature of the amorphous structure is conducive to homogeneous doping. Therefore, since charge and spin states are most sensitive to the local environment, local dopant moments existing in c-Si should also be observable in a-Si. Electrically doped a-Si resembles its crystalline counterpart in many aspects. For instance, a concentration-tuned metal-insulator (M-I) quantum phase transition can be achieved by doping, although the critical concentration $x_c$ increases by orders of magnitude due to strong disorder-driven localization (e.g. $x_c \sim 10^{-4}$ for doped c-Si [100] vs $10^{-1}$ for doped a-Si and/or a-Ge [33, 50, 87, 101]). a-Si has been successfully magnetically doped with rare earth ions with large magnetic moment, such as Gd (a-Gd$_x$Si$_{1-x}$). In this material, which has a half-filled 4f shell, strong moment-carrier interactions are demonstrated by magneto-transport measurements (a-Gd$_x$Si$_{1-x}$ showed enormous magnetoresistance MR$\sim 10^5$ at 1 K), which leads to a unique type of insulator-to-metal transition driven by magnetic fields in a-Gd-Si and a-Gd-Ge alloys [33, 50], similar to that seen in crystalline Gd$_{3-x}$Gd-Si$_4$ [4].

There have been limited reports about Mn-implanted a-Si (denoted as a-Si$_{1-x}$:Mn$_x$), mainly focusing on transport properties for $x \sim 0.07$-0.22 [102–104]. Samples were prepared by room-temperature Mn ion-implantation either into e-beam-evaporated a-Si on quartz ($x \leq 0.13$) [102] or into c-Si on sapphire with simultaneous amorphization of the films ($x > 0.13$) [103]. No magnetic properties were reported. However, a characteristic temperature was observed in the transport data, which was attributed to spin-glass (SG) ordering by d-d spin correlation between Mn atoms. The characteristic SG temperatures ($T_{SG}$) were not confirmed by magnetization measurements, but were estimated from the cross-over temperature between a variable-range hopping (VRH) behavior and a simple activated behavior obtained from dc conductivity data fitting. From this analysis, $T_{SG}$ was claimed
to vary from 6 to 20 K, depending on the Mn concentration. This $T_{SG}$ is rather high, comparable to that found in amorphous MnSi ($x=0.5$), with SG freezing at $T_f=22$ K. Such high $T_{SG}$ requires a local Mn moment with $d$-$d$ exchange interactions. These results were explained by AFM ordering of small magnetic clusters and magnetic polaron formation within the Mn clusters. The $a$-Si$_{1-x}$:Mn$_x$ films undergo an $M$-$I$ transition at a similar critical composition ($x_c\sim0.137$ [104]) as for $a$-Gd$_x$Si$_{1-x}$, but there is no large MR effect [102]; the obvious difference is $d$ vs $f$ electron magnetism. The MR must be related to an exchange interaction between carriers and moments. Therefore, it is puzzling that MR would be smaller in a material with $d$ electrons ($a$-Mn-Si) than one with $f$ electrons ($a$-Gd-Si) since $s$-$d$ exchange is typically much larger than $s$-$f$ exchange.

Ludwig and Woodbury have developed a model to predict the spin and charge states of 3$d$ transition metals within $c$-Si [35]. The Ludwig-Woodbury (LW) model states that crystal-field splitting ($\Delta_{CF}$) is small in $c$-Si compared to the on-site exchange energy ($\Delta_{EX}$), so that all 3$d$ impurities have a maximum spin value (Hund’s rule). The LW model was later challenged for the early and late transition metals such as Ni and Ti, but is still believed to account for Mn impurities. Electron-spin resonance (ESR) experiments confirmed the spin states of four different charge states for interstitial Mn ($\text{Mn}^+_I$, $\text{Mn}^0_I$, $\text{Mn}^+_I$ and $\text{Mn}^{2+}_I$) [98], all consistent with the LW model. The 4 nearest neighbors (tetrahedral symmetry) and the 6 second nearest neighbors (octahedral symmetry) of an interstitial site in $c$-Si are very close together and thus both sets of neighbors take part in determining $\Delta_{CF}$. This splits the $d$ levels into $e$ and $t_2$ levels, with $e$ levels lying higher than $t_2$ levels. Spin states of the two possible substitutional states ($\text{Mn}^\pm_{Si}$ and $\text{Mn}^{2\pm}_{Si}$) proposed by the LW model have not been observed by ESR measurements, but would have $J=S=1$ and $J=S=5/2$, respectively. The $t_2$ levels lie higher than the $e$ levels for both $\text{Mn}^\pm_{Si}$ states. In $a$-Si, the site symmetry is lowered due to disorder and usually leads to a uniaxial symmetry with random orientations. This may lead to larger $\Delta_{CF}$. Meanwhile, $\Delta_{CF}$ also depends on the covalency/ionizability of the Si. The effect on the crystal field splitting due to the disorder is unknow, but is speculated to be small due to the Si covalency.

We report here on Mn-doped amorphous silicon ($a$-Mn$_x$Si$_{1-x}$) thin films, with
between 0.005 to 0.175, covering both the dilute and the M-I transition regions.
The films were prepared by $e$-beam co-evaporation of Mn and Si under ultrahigh vacuum (UHV) conditions. Co-deposited $a$-Mn$_x$Si$_{1-x}$ samples have a much more homogeneous Mn distribution in the $a$-Si matrix compared to that of implanted samples, and should thus provide a better representation of the behavior of this type of amorphous solid solution. The focus of this current work is to understand the magnetic and magneto-transport properties of Mn dopants in $a$-Si, especially the presence or absence of any local Mn moment and its effect on electrical transport.

6.2 Experimental Details

The $a$-Mn$_x$Si$_{1-x}$ samples were grown by $e$-beam co-evaporation of high purity Si and Mn sources onto substrates held near room temperature (below 60 °C during film growth). This condition is in contrast to the film preparation described in Refs. 16 and 19, where the substrates were held at ∼350 °C to avoid amorphization, and post-implantation annealing (up to 800 °C) was used to create $c$-Si$_{1-x}$:Mn$_x$ films. Our base pressure prior to deposition was below 8×10$^{-10}$ Torr. Thickness monitors were used in situ for each source during deposition in order to precisely control the real-time Mn and Si flux to achieve uniform doping profiles as well as the desired Mn concentrations. The film compositions and lack of oxygen impurities were determined by RBS, using oxygen-resonance energy to enhance sensitivity, and by high-resolution cross-sectional transmission electron microscopy (HR-XTEM). Magnetic and magneto-transport measurements were made with a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. Further details can be found in Ref. 25. XAS data were taken at the Advanced Light Source (ALS) beam line 6.3.1, Lawrence Berkeley National Lab. Signals were collected in total electron yield (TEY) mode. All measured thin film samples, including the reference sample of a pure Mn metal film, were capped with 20~40 nm Al and stored in a vacuum desiccator to avoid oxidation. Commercially available Mn oxide powders with different Mn valences (MnO, Mn$_2$O$_3$ and MnO$_2$, corresponding to $d^5$, $d^4$ and $d^3$ configurations) were used as standards as well.
6.3 Experimental Results

6.3.1 Materials and Structural Characterization

Figure 6.1: (a) Low resolution XTEM micrograph; arrows specify columnar structure and growth direction; (b) HR-XTEM micrograph, (c) diffractogram data and (d) EDX profile for \(a\)-Mn\(_{0.11}\)Si\(_{0.89}\). The scale bars are 10, 2, 2 nm in (a), (b) and (c) respectively.

Figure 6.1 shows HR-XTEM analysis for a typical \(a\)-Mn\(_x\)Si\(_{1-x}\) film, where \(x=0.11\). The film shows columnar morphology in the growth direction, a typical feature for low \(T\) thermally evaporated thin films [25], with column diameters \(\sim\)10 nm [Fig. 6.1(a)]. The physical transport and magnetic properties were shown experimentally to not depend on microstructure at this length scale in amorphous Gd-Si alloys prepared by the same growth technique [25]. The \(a\)-Mn\(_x\)Si\(_{1-x}\) films appear to be amorphous with no significant sign of phase segregation or nanocrystallites. Figure 6.1(b) shows a slight suggestion of lattice fringes for regions of less than 2 nm; but digital diffractograms show typical amorphous rings, indicating absence of long-range ordering [Fig. 6.1(c)]. Annular-dark-field (ADF) images with energy-dispersive X-ray (EDX) spectroscopy were also used to probe the homogeneity of the \(a\)-Mn\(_x\)Si\(_{1-x}\) films. As an example, Fig. 6.1(d) shows the variation
of Mn and Si counts along a 250 nm line parallel to the film surface. The Mn
distribution was uniform along the scanning length, with no strong indication of
significant fluctuation in Mn concentration within the measurement uncertainties.

![Figure 6.2: (Color) O resonance RBS data for a-Mn_{0.08}Si_{0.92}. All other samples show the same trend. Mg_{sub} and O_{sub} are signals from the MgO substrate. O_{Res} is the O resonance signal.](image)

Figure 6.2: (Color) O resonance RBS data for a-Mn_{0.08}Si_{0.92}. All other samples show the same trend. Mg_{sub} and O_{sub} are signals from the MgO substrate. O_{Res} is the O resonance signal.

Figure 6.2 shows RBS spectra for a typical a-Mn_{x}Si_{1-x} film (x=0.08). Film compositions were obtained from data simulations with error bars of ∼0.001 and 0.005, for Si and Mn, respectively. Oxygen-resonance spectroscopy was used to probe specifically for oxygen contamination (the oxidation enthalpy of Mn is high compared to Si, and would counteract Mn doping and alter the Mn magnetic properties). A {4He}^{2+} ion beam with O resonance energy (E_{Res}=3.05 MeV) was used and oxygen-resonance RBS peaks (labeled as O_{Res} in Fig. 6.2) were observed at ∼1.1 MeV, indicating a surface oxide layer. By slightly increasing E_0 above E_{Res}, oxygen content below the film surface could be probed (the oxygen resonance occurs when the {4He}^{2+} kinetic energy is reduced to 3.05 MeV after penetrating to
a depth below the film surface). If $O_{\text{Res}}$ were observed over a range of $E_0 > E_{\text{Res}}$, it would have indicated oxygen contamination throughout the film. Here, however, the $O_{\text{Res}}$ peak intensity is reduced and eventually disappears after $E_0$ is increased above $E_{\text{Res}}$, as shown in Fig. 6.2. We can therefore conclude that O is only located near the film surface, within less than a few nm, which is small compared to the total film thickness (∼400 nm).

The room-temperature (RT) conductivity ($\sigma_{\text{RT}}$) of the films as a function of time ($t$) after exposure (with the first data point taken within 40 min) to air from vacuum was monitored and found to be stable up to at least 200 hours. The slightly reduced $\sigma_{\text{RT}}$ (≤4%) for this time period is probably due to a thin self-limiting oxide layer, which is insulating and thus reduces the effective thickness of the film. For this 4% reduction, the estimated thickness of this oxide layer is less than 10 monolayers, in good agreement with the RBS O resonance data reported above.

Figure 6.3 shows the total atomic number density ($n_{\text{total}}$) for $a$-Mn$_x$Si$_{1-x}$ samples with different $x$, obtained by dividing the RBS areal density by the film thickness, as measured by atomic force microscopy. Since the structure of high quality $a$-Si is a continuous random network (CRN), which preserves the local $sp^3$ tetrahedral covalent bonding, with small deviations in bond length and bond angle, the $n$ for $a$-Si should be comparable to that of $c$-Si [25]. Undoped $a$-Si with 98% number density of $c$-Si is achieved by $e$-beam evaporation [23]. In Fig. 6.3, the $n_{\text{total}}$ of $a$-Mn$_x$Si$_{1-x}$ increases with $x$, as opposed to results in the literature for crystalline $c$-$X_{1-x}$:Mn$_x$ ($X$=Si, Ge), where substitotional Mn were found to decrease $n_{\text{total}}$ (i.e. increase the lattice constant) because of lattice strain caused by the larger radius of Mn atoms [15, 105, 106].

### 6.3.2 Conductivity and Magnetization

Figure 6.4 shows the dc conductivity ($\sigma_{\text{dc}}$) vs $T$ for different $x$. The conductivity has a positive temperature coefficient and increases monotonically with the level of Mn doping, indicating semiconducting behavior and the effect of Mn doping in $a$-Si. The increasing $\sigma_{\text{dc}}$ with increasing $T$ is also a signature of localization in
Figure 6.3: (Color) Total atomic number density ($n_{\text{total}}$, obtained by dividing RBS areal density by film thickness), including both Mn and Si, as a function of $x$. For comparison, dotted line is the calculated $n_{\text{total}}$ assuming all doped Mn go in interstitially without affecting the $a$-Si number density; dash-dot line is the calculated $n_{\text{total}}$ assuming the same fraction of Mn are totally phase segregated into metal clusters in $a$-Si [number density of pure $a$-Si ($4.97 \times 10^{22}$ /cm$^3$) and Mn metal ($7.96 \times 10^{22}$ /cm$^3$) are used]. If Mn were substitutional, then $n_{\text{total}}$ should remain at the undoped $a$-Si number density (or even decrease due to the larger expected covalent radius), contrary to observation.
Figure 6.4: (Color) $\sigma_{dc}$ vs $T$ for $a$-Mn$_x$Si$_{1-x}$ measured by standard four-point probe method on lithographically defined Hall ball geometry. Inset shows the same plot on log-log scale to make the insulating behavior for the $x=0.04$, 0.095, and 0.135 samples clear.
Figure 6.5: (Color) ZFC $\chi(T)$ data for $a$-$\text{Mn}_{0.135}\text{Si}_{0.865}$, measured on heating in an 10 kOe dc magnetic field after cooling the sample in zero field. FC $\chi(T)$ is identical. Other concentrations fit similarly, but with $p_{\text{eff}}$ dependent on $x$. Solid lines are the fit to the CW law.

a disordered electronic system. A concentration-tuned $M$-$I$ transition is visible; samples are insulating for $x \leq 0.135$, whereas they are metallic for higher $x$. The 0.135 sample is very close to $x_c$ but slightly on the insulating side. This result is in good agreement with the $x_c=0.137$ found in Mn-implanted $a$-Si samples [104].

Magneto-transport properties were measured for one sample on the insulating side ($x=0.135$) and one sample on the metallic side ($x=0.175$). A small positive MR was found down to 2 K at $H=70$ kOe for both samples, 27% and 16% for $x=0.135$ and $x=0.175$, respectively, which can be attributed to the electron correlation effect in disordered non-magnetic electronic systems [46]. Yakimov and coworkers found a crossover from small positive MR to small negative MR below 2.3 K (-25% at 1.76 K and 4.5 T) for a Mn-ion-implanted $a$-Si sample ($x=0.11$) held at room temperature for 8 years [102]. We did not observe any negative MR in our samples. The negative MR found in Ref. 102 was attributed to magnetic clusters.

Figure 6.5 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetic
susceptibility $\chi(T)$ data recorded in a dc magnetic field of 10 kOe. For $x=0.04$, which had the largest raw magnetic signal, ZFC and FC susceptibilities were also measured in smaller fields ($H=1000$ and 350 Oe). All $\chi(T)$ curves were identical and showed no splitting between ZFC and FC. 10 kOe is a large field for measuring $\chi$ and the reduction in $\chi$ from the true low field value is $\sim 20\%$, leading to a 10% underestimation of the effective moment ($p_{\text{eff}}$). This high field is necessary to obtain reliable sample signals (strongly $T$ dependent) above the diamagnetic background signal (negligible $T$ dependent) for our samples, all of which show very small magnetic signals. The diamagnetic background from the Si$_x$N$_{2-x}$ coated Si substrate was measured separately for each $T$ and $H$, as was an undoped $a$-Si control sample prepared using the same Si evaporation batch. The resulting net $a$-Mn$_x$Si$_{1-x}$ response followed the Curie-Weiss (CW) law very well with a very low CW temperature ($|\theta|<2$ K). No ferromagnetic or SG states were observed in the temperature range between 2-40 K. Above 40 K, the error bars were large due to the small signal. The thermoremanent moment (TRM) was obtained by cooling the sample in a field of 70 kOe and then measuring the TRM on heating the sample in zero magnetic field from 1.9 K to 380 K; no significant signal was obtained at any temperature for any of the samples. These results indicate that the magnetic signal is purely paramagnetic.

Figure 6.6(a) shows $M$ (magnetization per Mn atom) vs $H$ at 2 K, assuming that all Mn atoms contribute equally to the signal. The diamagnetic background from the substrate was again subtracted. No hysteresis loop is found. $M$ decreased very fast with the Mn concentration. If it is assumed that either $J=1$ or $5/2$ for $x=0.005$, then 92% or 37% of the Mn atoms are magnetically active, respectively. The $M$ vs $H$ data for all samples scale well to a Brillouin function for free magnetic ions, as shown in Figure 6.6(b). The value of $M$ at 6 kOe should be within 2% of the saturation moment for non-interacting Mn ions (whether $J=1$ or $5/2$), and so its value can be used to calculated the saturation moment per Mn atom ($p_{\text{sat}}$) as a function of $x$.

Figure 6.7 shows the Mn concentration dependence of the $p_{\text{eff}}$ as taken from the CW fitting constant $A=n_{\text{Mn}}p_{\text{eff}}^2B^2/3k_B$ with $n_{\text{Mn}}$ from RBS, and of the $p_{\text{sat}}$ as taken from $M$ at $T=2$ K, $H=6$ kOe shown in Fig. 6.6. Both $p_{\text{eff}}$ and $p_{\text{sat}}$ decrease
Figure 6.6: (Color) (a) Magnetization per Mn atom in units of $\mu_B$ vs. $H$ for different Mn concentration at 2 K, assuming all Mn equally contribute. Inset shows same data on expanded scale. Lines are guides to the eye. (b) Normalized $M$ vs $H$ for various compositions $x$ at 2 K. Lines show Brillouin function for $J=S=5/2$ and $J=S=1$ (the two states suggested for interstitial Mn in Si) for comparison.
sharply from $x=0.005$ to $x=0.04$, becoming very small and decreasing smoothly with increasing Mn concentration.

![Graph showing $p_{\text{sat}}$ and $p_{\text{eff}}$ as functions of Mn concentration.]

Figure 6.7: (Color) $p_{\text{eff}}$ (extrapolated from $A = n_{\text{Mn}}^2 p_{\text{eff}}^2 \mu_B^2 / 3k_B$ obtained by the CW fitting) and $p_{\text{sat}}$ (calculated from $M_{\text{sat}} = n_{\text{Mn}} p_{\text{sat}}$ with $M_{\text{sat}}$ taken from $M$ at $T=2$ K, $H=6$ kOe shown in Fig. 6.6) for different Mn concentrations. $n_{\text{Mn}}$ is the total Mn number density. Lines are guides to the eye.

6.3.3 Electronic Structure by XAS

Figure 6.8 shows XAS spectra for all the samples including the references. The atomic multiplet features of the Mn ions in oxides can be well resolved with the beam line setup at a resolution of $\pm 0.1$ eV. The drift of the X-ray energy as a function of time is also found to be small $\sim \pm 0.1$ eV. Multiplets were confirmed with standard atomic multiplet simulations [60]. We use the well-known $L_3$ maximum of the Mn$^{2+}$ as our energy reference which occurs at 639.0 eV in our data (Fig. 6.8(i); the MnO powder was found to be not pure but in a mixture with Mn$_2$O$_3$. Nevertheless, the sharp absorption peak at 639.0 eV comes from Mn$^{2+}$). All other XAS spectra including the simulated ones are calibrated with respect to this energy. The XAS spectra of $a$-Mn$_x$Si$_{1-x}$ in general has very broad $L_3$ and $L_2$ peaks and
Figure 6.8: XAS of Mn L edges for different samples and standards. $\alpha$-Mn$_x$Si$_{1-x}$ and $\alpha$-Mn$_x$Ge$_{1-x}$ were prepared by $e$-beam coevaporation and the Mn metal film was prepared by magnetron sputtering at 4 mTorr, all with room temperature substrate temperatures. $\alpha$-Mn$_x$Si$_{1-x}$ and the Mn metal samples were capped in situ with 20~40 nm Al. Mn oxides are commercially available chemical powders. All samples shown here are stored in vacuum desiccators. Uncapped $\alpha$-Mn$_x$Si$_{1-x}$ samples stored under ambient conditions (not shown here) gradually develop (time scale of months) a small feature at 639.0 eV due to surface oxidation.
no XMCD signal is observed, consistent with the paramagnetic behavior of these samples. The spectra of metallic Mn and $a$-Mn$_x$Si$_{1-x}$ both show no distinct atomic multiplets, but they differ from each other in peak positions and peak widths. The XAS $L$ edges of the Mn metal have lower energy and narrower line width. Lastly, the branching ratio of the $a$-Mn$_x$Si$_{1-x}$ (defined by $\int L_3/(\int L_2+\int L_3)$ ratio, where $\int L_2$ and $\int L_3$ are the integrated intensities of the $L_2$ and $L_3$ white lines, respectively, after edge jumps at both edges are removed) is 0.62, much smaller than that of non-interacting $d^5$ high spin states ($\sim 0.8$) [107]. The branching ratio for Mn with a nearly half-filled 3$d$ shell is related to electrostatic interactions and is very sensitive to the change in the electronic structure. The $d^5$ high-spin state has the maximum branching ratio of $\sim 0.8$, while bulk Mn is 0.73 when assuming a mixed Mn states of $d^5$, $d^6$ and $d^7$ [108].

Figure 6.9 shows the detailed analysis of the $L_3$ edges of $a$-Mn$_x$Si$_{1-x}$. For the three high Mn doping samples ($x \geq 0.04$), the absorption intensity and line shape scale very well with $x$. After normalizing to the concentration-dependent post-edge steps, the spectra for these three samples collapse extremely well as shown in the inset of Fig. 6.9. However, the $x=0.005$ sample obviously does not scale and exhibits a different line shape. The main plot of Fig. 6.9 focuses on the $L_3$ edges, with normalized peak heights in order to show the differences in line shape, including the peak positions and peak widths. For the $x=0.005$ sample, the $L_3$ peak is at 639.0 eV, shifted 0.9 eV lower in energy with smaller broadening as compared to the other samples. We, however, note that this feature at 639.0 eV aligns well to the major Mn$^{2+}$ $L_3$ peak found in MnO as marked in Fig. 6.8.

Besides the 639.0 eV peak, $L_3$ edge of the $x=0.005$ sample also shows a broad shoulder with a peak at $\sim 640.0$ eV. This strongly suggests that the spectrum is due to a mixture of Mn states. Fig. 6.10 presents the results of a superposition of possible states existing in the $x=0.005$ sample. The two candidates are the Mn$^{2+}$ spectrum [with the peak at 639.0 eV, Fig. 6.10(d)] and the Mn XAS spectrum found in high Mn concentration samples [Fig. 6.10(a)]. The previous magnetization studies have shown that only a tiny concentration of magnetic Mn$^{2+}$ centers ($\sim 10^{-3}$) are present in all $a$-Mn$_x$Si$_{1-x}$ samples. For the $x=0.005$ sample the Mn$^{2+}$ fraction was found to be 35% as will be discussed later. The remaining 65% of the
Figure 6.9: (Color) $L_3$ edges of all $a$-Mn$_x$Si$_{1-x}$ samples. Spectra were normalized to the $L_3$ peak height to illuminate the difference in peak positions and peak widths. Inset shows the spectra normalized to the post-edge jumps to show how the overall line shapes of both $L_3$ and $L_2$ scale with $x$.

Figure 6.10: The demonstration of mixed Mn states in the $x=0.005$ sample (curve c) by superposition of the $L_3$ edge of Mn$^{2+}$ (curve d) and the $L_3$ edge of the $x=0.18$ sample (curve a).
Mn dopants are magnetically silent, as in the other high Mn concentration samples which only show broad XAS peaks. Using these two percentages to weight the corresponding XAS spectra, the linear combination shown in Fig. 6.10(b) reproduces all the features of the measured spectrum of the $x=0.005$ sample shown in Fig. 6.10(c).

6.4 Discussion

As shown in Fig. 6.3, the total atomic number density $n_{\text{total}}$ increases with Mn doping. This is comparable to, or slightly higher than, the calculated $n_{\text{total}}$ (also plotted in Fig. 6.3) assuming all Mn are at interstitial sites without changing the $a$-Si matrix density, suggesting that Mn atoms act as interstitial dopants in $a$-$\text{Mn}_x\text{Si}_{1-x}$ (therefore are at sites with high Si coordination number and low symmetry). Mn$_\text{Si}$ on the other hand would keep $n_{\text{total}}$ constant. The charge and spin states of Mn strongly depend on the local environment. Preliminary ESR results on our films show $g = 2.01 \pm 0.03$ for Mn, indicating Mn is in a pure spin state. Based on the LW model proposed for Mn in Si, there are two possible interstitial Mn sites with quenched orbital moment: one is Mn$^{2+}_1$ (3$d^5$, $J=S=5/2$) and the other is Mn$^{-1}_1$ (3$d^8$, $J=S=1$).

The small magnetization (both $p_{\text{eff}}$ and $p_{\text{sat}}$) of all samples suggests that only a very small fraction of Mn atoms are magnetically active. Based on the saturation moment, we can obtain the fraction of magnetically active Mn ions (denoted as $c_m$) assuming $J=S=1$ or 5/2. For a pure paramagnetic state, the same magnetic centers contribute to $\chi(T)$. The atomic moment ($gJ$) and the effective moment ($g\sqrt{J(J+1)}$) are connected for a specific $J$ value, with $g=2$ from ESR data. We re-calculate the new effective moment (now denoted as $p_{\text{eff}}^m$) based on $c_m n_{\text{Mn}}$ (instead of $n_{\text{Mn}}$ in Fig. 6.7) and the measured CW constant $A$. For $J=S=1$, the resulting $p_{\text{eff}}^m$ values are more than 20% greater than the theoretical value of 2.83 $\mu_B$. $\chi$ was determined with a 1 kOe field, which leads to smaller $\chi$ than determined at lower field, thus underestimating of $p_{\text{eff}}^m$. This indicates that $J=S=1$ is not the correct spin state. For $J=S=5/2$, the resulting $p_{\text{eff}}^m$ values are ~10% smaller than the theoretical value of 5.92 $\mu_B$. We can check the underestimation of $p_{\text{eff}}^m$ by
using the Brillouin function for $J=S=5/2$ moment at 2 K. Since $p_{\text{eff}} \propto \sqrt{A} \propto \sqrt{\chi}$, the fractional reduction $\Delta p_{\text{eff}} / p_{\text{eff}} \propto \sqrt{\chi}$ from using 1 kOe instead of the low-field limit is $\sim -20\%$, which gives $\Delta p_{\text{eff}} / p_{\text{eff}} \sim -10\%$. Taking this $-10\%$ deviation into account, $p_{\text{eff}}^m$ and $p_{\text{sat}}$ are in excellent agreement for $J=S=5/2$.

In Table 6.1, we summarize all of the fitting parameters as well as the estimated $c_m$ and $p_{\text{eff}}^m$. The agreement between the atomic moment and the effective moment for all $x$ values strongly suggests that Mn$^{2+}$ ($3d^5$, $J=S=5/2$) are the magnetically active sites in these films, but only account for a small fraction of the total doping (e.g. $c_m=0.6\%$ for $x=0.175$).

The decreasing moment seen in Fig. 6.7 can be explained by the decrease of $c_m$ with $x$. $c_m$ are 35.2% and 5.6% for the $x=0.005$ and 0.04 films, respectively, and become less than 1% when $x \geq 0.12$ (as shown in Table 6.1). The rest of the Mn atoms are in a non-magnetic state and contribute to the transport properties only (as shown by the increase of $\sigma_{dc}$ with $x$).

These two types of Mn states found in $a$-Mn$_x$Si$_{1-x}$ are in sharp contrast to the situation for $a$-Gd$_x$Si$_{1-x}$, where all Gd atoms are in Gd$^{3+}$ states, contributing $3e^-$ as well as 7 $\mu_B$ moment (due to the half-filled $f$ shell, $J=S=7/2$) per Gd. The dual role of Gd is the key to its SG ground state as well as the enormous negative MR in the magnetically doped amorphous semiconductor studied previously [25]. In $a$-Mn$_x$Si$_{1-x}$, only a tiny percentage of the Mn sites are magnetically active and therefore far separated, and thus no magnetic interaction is developed as in $a$-Gd$_x$Si$_{1-x}$. The majority of Mn atoms are in a non-magnetic state (which is not predicted by the LW model), despite contributing to transport. The small positive MR is consistent with this result, as in other non-magnetic disordered systems [46]. We do not observe any negative MR in our co-deposited $a$-Mn$_x$Si$_{1-x}$ films even for samples on the insulating side, contrary to what was reported previously for Mn-implanted samples [102].

The excellent consistency between the XAS data and the magnetization results further strengthen the two-state model we have proposed for $a$-Mn$_x$Si$_{1-x}$. The revealing feature is the nonmagnetic state associated with the broad XAS absorption peaks, since such states are not predicted by existing calculations. Thus the physical origin of the XAS line shape broadening is worth discussing here. The dis-
order in $a$-Si may affect the local symmetry and crystal field (CF) splitting of the Mn sites. However, as discussed previously, the local tetrahedral bondings should still be preserved in $\varepsilon$-beam evaporated $a$-Si. Moreover, the CF should be a small effect in Si according to the Ludwig-Woodbury (LW) model [35], which states that Hund’s rule is still valid for Mn $d$ shell in Si and favors high spin states. CF at Mn sites in oxides provides an upper bound estimate of CF strength in Si, which is found to be $<$1 eV according to XAS atomic multiplet simulations. CF within this small energy range only has minor effects on the atomic XAS spectra: $\sim$0.5 eV shift of the peak positions and no significant peak splitting. Thus even if one has a random distribution of CF strengths due to disorder, linear combinations of weighted simulated spectra corresponding to different CF splitting does not yield the smooth broad XAS absorption observed in the experimental data.

Mixed Mn valence states can lead to significant XAS broadening, such as found in (La, Ca)MnO$_3$ (LCMO) and MnSi crystalline compounds. The $L$-edge broadening is due to the co-existence of the Mn$^{3+}$ and Mn$^{4+}$ sites for the LCMO [62], and is proposed to be the mixed valence ground state of different $d$ multiplets for MnSi [109]. However, one can still recognize the underlying features from the atomic multiplets in these examples. More importantly, all known Mn atomic valence states should still have a local moment, which should be detected by the magnetization measurement.

In a $p$-$d$ hybridization scenario, as for the well-studied FM Ga$_{1-x}$Mn$_x$As DMS material, XAS of Mn at substitutional As sites still possesses significant multiplet features at the $L$ edges [110] as well as large Mn moments approaching the atomic values ($\sim$4.5 $\mu_B$), indicating $p$-$d$ hybridization are dominated by $d$ characteristics. Covalency of Mn-Si bonds is stronger than that of Mn-As bonds, thus $d$ electrons could lose their $d$ characteristic due to strong screening by the Si $p$ states. However, substitutional Mn in Si has a tetrahedral environment so that at most four $d$ electrons are used for covalent bonding, thus the remaining three $d$ electrons are still expected to have spin moments of 3 $\mu_B$ according to the LW model and first principles calculations [14,35].

How would the amorphous matrix affect the local moment of the Mn$_I$ sites in $a$-Si compared to the $c$-Si case? Mn$_I$ sites in $c$-Si do not form covalent bonds
with Si and are always predicted to have local moments. This should be the same case in $a$-Si. However, if any local moment exists in our $a$-MnxSi$_{1-x}$ films, for the wide concentration and the temperature range measured, one would not expect a purely paramagnetic response with small $\theta$ values and no sign of any magnetic interaction. It is possible but unlikely that local moments exist but are completely canceled because of very strong Mn-Mn AFM interactions, since AFM ordering is not robust to disorder and should lead to a magnetic freezing state, such as a SG phase (with $T_f$) or a clustered spin glass (with blocking temperature, $T_B$), showing magnetic hysteresis (differences between FC and ZFC states) and TRM. $T_f$ or $T_B$ should increase with the magnetic concentration, but no magnetic freezing was observed for $x$ up to 0.175. It is possible that $T_f$ and $T_B$ are so high that samples are already in a frozen state at 40 K and thus only express a very small moment. However, the known concentrated SG $a$-MnSi (1:1 stoichiometry) has a $T_f$ only at 22 K [111], while the CW behavior of our samples is reliably measured up to 40 K, as shown in the inset of Fig. 6.5 (above 40 K, the signal is too small with large error bars). $T_f$ of this $a$-MnSi is smaller but comparable to the magnetic ordering temperature ($T_C=30$ K) of its crystalline counterpart, the compound MnSi, which has a helical spin structure with $\sim$18 nm wavelength. Above $T_f$ or $T_C$, in the paramagnetic states, they have comparable $p_{\text{eff}}$, which are 2.2 and 2.6 $\mu_B$ for the compound MnSi and $a$-MnSi respectively [112]; both of these states would give significantly larger $\chi$ than observed at 40 K.

If there were non-interacting Mn complex clusters in $a$-Si (invisible in HR-XTEM), such as Mn dimers or trimers, which could be AFM-coupled, showing zero moment. Such complexes have not been experimentally observed to the best of our knowledge, and are theoretically found to have higher energy than the FM-coupled configuration, and so are unlikely to be causing the lack of magnetism in $a$-MnxSi$_{1-x}$ [113, 114]. Furthermore, only the neutral charge state of Mn$_{I}$ favors AFM coupling in Si, which should therefore not contribute to the transport [113]. Mn$_{II}$ [35] and [Mn$_{III}$$^{2+}$-Mn$_{I}^{-}$] [115] clusters have large $S$ values, thus not the case here. Existence of metallic Mn or Mn-rich clusters of larger scale are not supported by the HR-XTEM results (shown in Fig. 6.1) and the atomic density analysis (shown in Fig. 6.3). Moreover, ferromagnetic clusters (even if not long range ordered but
superparamagnetic) should result in an enhanced $p_{\text{eff}}$, opposite to what we have seen. All these strongly indicate the majority Mn atoms enter into a non-magnetic doping environment in $a$-Si, forming even at $x$ as low as 0.005 (~$64.8\%$).

The totally quenched Mn moment in $a$-Si is intriguing and needs more understanding. In our two-state scenario, we have argued that the small magnetic signal is due to a small fraction of Mn$^{2+}$ sites according to the LW model, while the majority of Mn atoms are in a totally non-magnetic state. Based on the comparable (high) atomic number density and the CRN model for $a$-Si, the local site symmetry should be only slightly perturbed for these Mn$_1$ when $x$ is small, and thus the LW model is still valid at least for low $x$. If adding more Mn enhances the crystal field splitting such that it overrules the LW model and Hund’s rule, a zero moment state could arise (Mn$^{+}_1$ with filled $t_2$ levels, or Mn$^{3+}_1$ with filled $e$ levels, dependent on which is lower), although such charge states should have multiplets at the $L$ edges in XAS measurement due to unfilled $d$ levels.

The smooth and broad $L$ edges of $a$-Mn$_x$Si$_{1-x}$ are most likely due to the formation of an itinerant impurity band. Film atomic density obtained from RBS and film thickness measurements increases linearly with the Mn doping $x$, suggesting that Mn are more likely at interstitial-like positions in $a$-Si matrix or positions with high Si neighbors such as in the crystalline Mn$_{15}$Si$_{26}$ silicide [116]. In both cases, the large number of Mn centers and Mn-Si covalent bonds can lead to delocalized states and the formation of an itinerant impurity band. Moments associated with itinerant bands are usually very small, if present at all, such as in the crystalline Mn$_4$Si$_7$ silicide [117]. The existence of itinerant states in insulating samples is explained by Anderson localization in this strongly disordered amorphous material. States in this band are localized due to disorder when $x \leq x_c$, and delocalized when $x > x_c$. For $x \ll x_c$, the localization length should be short, but may still exceed the Mn-Mn distances. These localized itinerant states should have no moment, similar to what is seen in the metallic crystalline Mn silicides.

It would be useful to evaluate how disorder affects the charge and spin states of Mn using first-principles calculations. If the analog of the local environment between $a$-Si and $c$-Si is valid, and since the local moment is largely determined by the local environment, then Mn would be expected to be in an interstitial site with
\( J=S=5/2 \). However, our results indicate almost no moment for Mn, suggesting a new state for Mn in \( a \)-Si, which is not predicted by any existing model for Mn in \( c \)-Si.

### 6.5 Conclusion

In conclusion, an unexpected quenched Mn moment state has been observed, forming at the lowest \( x \) studied \((5 \times 10^{-3})\), which is not predicted by any existing model for transition metal dopants in Si. This result explains why MR for \( a-\text{Mn}_x\text{Si}_{1-x} \) is positive and small, with typical values for disordered non-magnetic electronic systems, unlike the enormous negative MR found in \( a-\text{Gd}_x\text{Si}_{1-x} \). The non-magnetic state is most likely due to the formation of an impurity band, subject to localization effects. The existence of the itinerant state is related to the local short-range Mn-Si covalency, and may explain why the quest for discovering intrinsic DMS based on Mn-doped Si has not been successful compared to Mn-doped III-V compound semiconductors. Our results also suggest that there is a concentration limit \((x \sim 10^{-3})\) where the LW model for Mn in Si is no longer valid.

### 6.6 Acknowledgement

Chapter 6, in part, contains the materials for future submission by Li Zeng, Erik Helgren, Maryam Rahimi, Frances Hellman, Rafiqul Islam and David J. Smith (2007). The dissertation author is the primary author of these papers.
Table 6.1: Sample composition, Curie-Weiss parameters and magnetic moment analysis for $a$-Mn$_x$Si$_{1-x}$ based on two different methods of treating the fraction of magnetically active Mn.

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<th>$\theta$</th>
<th>$A$</th>
<th>$p_{\text{eff}}$</th>
<th>$p_{\text{eff}}/p_{\text{sat}}$</th>
<th>$c_m$</th>
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1From RBS and AFM measurements.

2$\theta$ and $A$ from CW fit: $\chi = A/(T - \theta) + b$; $b$ is a small temperature-independent constant due to combined core, and magnetometer background contributions.

3$p_{\text{eff}}$ per Mn obtained from $A = n_{\text{Mn}}c_m^2\mu_B^2/3k_B$; $p_{\text{sat}}$ per Mn obtained from saturation moment at 2 K and 6 kOe, both assuming all $n_{\text{Mn}}$ contribute equally, with $n_{\text{Mn}}$ from RBS.

4$c_m$ is the magnetically active Mn concentration obtained from saturation magnetization, assuming each active Mn has $J=S=5/2$.

5$p_{\text{eff}}^m$ is the calculated effective moment per active Mn atom based on $c_m$, each with $J=S=5/2$. 
Suggested Future Work

This chapter briefly describes possible future directions on magnetically doped amorphous semiconductors, including new preparation methods and new material systems to study the moment-carrier interactions. This chapter is divided into two sections: the first part discusses Gd-doped related systems and the second part discusses Mn-doped related systems.

7.1 Gd-doped Amorphous Semiconductor

The $a$-Si band gap can be tuned by C doping. This is well-known to the $a$-Si solar cell industry and has been used to increase the optical band gap of $a$-Si [118]. For the binary semiconductor matrix $\text{Si}_{1-y}C_y$, one can vary $y$ between 0 and 0.5. The $y=0.5$ crystalline end member is $\beta$-SiC, a face-centered cubic structure. Crystalline $\beta$-SiC has an indirect band gap of $\sim 2.1$ eV. SiC also has many other crystalline forms, such as the most common polymorph $\alpha$-SiC, a hexagonal structure. Crystalline $\alpha$-SiC has an indirect band gap of $\sim 3.0$ eV (0 K). Both $\alpha$ and $\beta$-SiC are considered wide band-gap semiconductors. The optical band gap of $\text{Si}_yC_{1-y}$ is found to increase with the C fraction $(1 - y)$ between the values of Si and $\beta$-SiC by theoretically calculation [119].

By incorporating Gd as the magnetic dopant into amorphous $\text{Si}_yC_{1-y}$, the resulting $a$-$\text{Gd}_x\text{Si}_yC_{1-x-y}$ film is a magnetically-doped amorphous ternary semiconductor. $x$ and $y$ can be independent tuned. By changing the ratio of $y$ over
1-x-y with the Gd concentration x fixed, one can study the matrix (band gap) dependence of the characteristic temperature $T^*$, which is found to be larger in $a$-Si than in $a$-Ge with the same Gd doping. This is believed to be due to the electron screening effect [33, 53]. The study of $a$-Gd$_x$Si$_y$C$_{1-x-y}$ would shed more light on this phenomenological model of $T^*$.

To prepare these ternary samples, we can use magnetron cosputtering as described in Chap. 3 and 4. Individual Gd, Si and C targets can be sputtered simultaneously by using the dc sputtering gun, the AJA Sparcle gun and the rf sputtering gun, respectively in the 5-gun AJA sputtering chamber.

We have learned from Chap. 5 that Gd implantation into ta-C at low temperatures leads to massive defects such as vacancies, interstitials and dangling bonds. These defects destabilize the metastable $sp^3$ bonds and lead to graphitization during the post-implantation annealing. One can possibly avoid these implantation damages by high-temperature implantation where dynamic annealing occurs, similar to the study of Ion-beam-induced transformation of diamond in Ref. 95. However, the reactivity of Gd with C at high temperature is unknown.

Another possible route to stabilize Gd in a $sp^3$-rich $a$-C matrix is to do ion-beam codeposition of Gd and C. The kinetic energy of C needs to be in an optimized energy window to favor $sp^3$ bond formation. In the literature, this energy window is $\sim 100$ eV, but could be affected by codeposition with Gd. The kinetic energy of Gd should be tuned (can be accelerated by a separate electrical field independently) to minimize its effect on the ta-C growth.

### 7.2 Mn-doped Amorphous Germanium

The quenched Mn moment in $a$-Si discussed in Chap. 6 is probably due to the Mn-Si covalency and the formation of an Anderson-localized impurity band with no local moment. This result is really unexpected since known models and calculations all indicate that Mn should have a local moment in the Si matrix [14, 35]. In Ref. 14, Mn moment in crystalline Si is calculated by ab initio full-potential augmented plane wave (FLAPW) electronic calculations. The total Mn magnetic moment is found to be 2.5-3 $\mu_B$ for Mn concentrations between 0.0625 and 0.5 in Si. In the
same paper, the total Mn moment is also calculated for the crystalline Ge matrix and the value is $\sim 3 \mu_B$ in the same concentration range, slightly but consistently larger than for the Si case. In analogy, it is interesting to see whether the Mn moment is robust in the $a$-Ge matrix or quenched as for the $a$-Si case.

For this purpose, two batches of $a$-Mn$_x$Ge$_{1-x}$ were made for preliminary magnetic, transport and magneto-transport measurements. For the first batch, the Mn was evaporated by the $e$-beam source and the Ge was evaporated in a Knudeson cell (K-cell). Samples were patterned afterward by photo lithography into Hall bar geometry for electrical measurements. It was found that even for a high Mn concentration sample $a$-Mn$_{0.18}$Ge$_{0.82}$, $\sigma_{dc}$ still showed insulating behaviors. There could be two possible reasons for the low conductivity: the K-cell was found to have a hot spot and was outgassing N$_2$ during the deposition. This probably led to a small amount of N incorporation, compensating the Mn doping. The second possibility is that during the photo lithography process, samples were heated up to 100 °C and this may have affected the film structure (note that at the end of the deposition, the sample plate temperature already reached 65 °C). However, these samples show spin glass freezing at low $T$ and a small negative MR, suggesting a possible different behavior of Mn in $a$-Ge than in $a$-Si. Later, a second batch of $a$-Mn$_x$Ge$_{1-x}$ films were made by $e$-beam coevaporation of both the Mn and Ge sources and no post-deposition process was performed. This batch (the $e$-beam batch) is believed to be free of contaminations, and the following discuss will be only focused on these samples.

Figure 7.1 shows the $\sigma_{dc}(T)$ of $e$-beam-evaporated $a$-Mn$_x$Ge$_{1-x}$ films. $\sigma_{dc}$ increases monotonically with the Mn concentration as in the $a$-Mn$_x$Si$_{1-x}$ case. This indicates successful electrical doping of Mn in $a$-Ge. An $x$-tuned $M$-$I$ transition is visible and the critical $x$ ($x_c$) is around $\sim 0.15$, very similar to $x_c$ found for $a$-Gd$_x$Si$_{1-x}$ and $a$-Gd$_x$Ge$_{1-x}$ ($x_c \sim 0.14$) and for $a$-Mn$_x$Si$_{1-x}$ ($x_c \sim 0.135$), although the underlying conduction mechanism ($s$ vs $d$ electrons and/or the valence electron density) could be quite different.

Figure 7.2 shows the dc susceptibility data for the $x=0.15$ sample. A clear split between the ZFC and FC data indicates a spin glass ground state. The same split was observed for samples with $x \geq 0.10$. The freezing temperature $T_f$,
Figure 7.1: (Color) dc conductivity ($\sigma_{dc}$) of $a$-Mn$_x$Ge$_{1-x}$ films for a wide range of concentration across the $M$-$I$ transition. Inset shows the same data on log-log scale.
Figure 7.2: (Color) Magnetization data for \(a\)-Mn\(_{0.15}\)Ge\(_{0.85}\) films measured both under zero-field-cooled (ZFC) and field-cooled (FC) conditions. Inset: effective moments determined from the paramagnetic state above the spin glass freezing state as a function of \(x\) for \(a\)-Mn\(_x\)Ge\(_{1-x}\).
estimated by the temperature where the split occurs, increases with $x$. More accurate determination of $T_f$ requires an ac susceptibility measurement. In the paramagnetic state, all susceptibility data fit the CW law very well. The effective moment $p_{\text{eff}}$ from the CW fit for all samples is shown in the inset of Fig. 7.2. Unlike $a$-Mn$_x$Si$_{1-x}$, a large $p_{\text{eff}}$ (~3-6 $\mu_B$) is seen.

Figure 7.3 shows the magnetic field dependence of magnetization $M(H)$ for all samples at 2 K. All the $M(H)$ data collapse on a single curve and fall well below the Brillouin function for non-interacting spin systems, whether $J=5/2$ or 1/2.

Figure 7.3: (Color) $M(H)$ per Mn for various $x$. Also shown is the non-interacting Brillouin functions for $J=5/2$ and 1/2.

The spin glass freezing and the unsaturated magnetization at high field and low temperature indicate that Mn has large local magnetic moments in $a$-Ge and there are strong interactions between them. $p_{\text{eff}}$ has a nontrivial $x$ dependence, which is different than the calculated results from Ref. 14. All these results are in sharp contrast to what were observed for $a$-Mn$_x$Si$_{1-x}$, where the majority of Mn are magnetically silent and cannot be detected by magnetization measurements.
While the $p_{\text{eff}}$ of $a$-$\text{Mn}_x\text{Si}_{1-x}$ decreases with $x$, the $p_{\text{eff}}$ of $a$-$\text{Mn}_x\text{Ge}_{1-x}$ increases with $x$ as shown in Fig. 7.4.

![Graph showing $p_{\text{eff}}$ for both $a$-$\text{Mn}_x\text{Si}_{1-x}$ and $a$-$\text{Mn}_x\text{Ge}_{1-x}$ as a function of Mn $x$.]

Figure 7.4: (Color) $p_{\text{eff}}$ for both $a$-$\text{Mn}_x\text{Si}_{1-x}$ and $a$-$\text{Mn}_x\text{Ge}_{1-x}$ as a function of Mn $x$.

The magneto-transport properties are closely related to the magnetic properties. In $a$-$\text{Mn}_x\text{Si}_{1-x}$, due to the lack of Mn local moment, MR is small and positive like typical nonmagnetic disordered systems. The existence of large local moments at doping sites is believed to be a necessary condition to have large MR for magnetically doped semiconductors, therefore it is not surprising that the MR of $a$-$\text{Mn}_x\text{Si}_{1-x}$ is small when the Mn moment is found quenched in $a$-Si. On the other hand, although $a$-$\text{Mn}_x\text{Ge}_{1-x}$ films appear to be having both charge carriers and local moments, current data show that only small MR for $a$-$\text{Mn}_x\text{Ge}_{1-x}$ is observed as shown in Fig. 7.5. The sign of MR, however, becomes negative in contrast to the positive MR in $a$-$\text{Mn}_x\text{Si}_{1-x}$. Comparing to $a$-$\text{Gd}_x\text{Si}_{1-x}$ films, the absence of large negative MR in $a$-$\text{Mn}_x\text{Ge}_{1-x}$ still needs more understanding.

Future experiments include HR-XTEM to look at the material structure and XAS study of the electronic structure of the $a$-$\text{Mn}_x\text{Ge}_{1-x}$ films. Clearly, Mn be-
Figure 7.5: (Color) MR comparison between $a$-$\text{Mn}_{x}\text{Si}_{1-x}$ and $a$-$\text{Mn}_{x}\text{Ge}_{1-x}$ samples.
haves quite different in $a$-Si than in $a$-Ge. The side-by-side comparison between them as well as comparisons to $a$-Gd$_x$Si$_{1-x}$ and $a$-Gd$_x$Ge$_{1-x}$ films are very important to answer the big question of what the sufficient conditions are to have large moment-carrier interactions thus large MR effects in magnetically doped semiconductors.
Bibliography


[34] A. I. Yakimov, A. V. Dvurechenskii, and C. J. Adkins. Effect of spin-glass
ordering on conduction in $a$-$Si_{1-x}$Mn$_c$ near the metal-insulator transition. 


[37] C. L. Chien, F. Y. Yang, Kai Liu, and D. H. Reich. Very large magnetoresis-
tance in electrodeposited single-crystal Bi thin films (invited). *J. Appl.

[38] P. B. Alers and R. T. Webber. The magnetoresistance of bismuth crystals


[40] F. Y. Yang, Kai Liu, C. L. Chien, and P. C. Searson. Large Magnetoresistance

[41] T. R. McGuire and R. I. Potter. Anisotropic magnetoresistance in ferromag-

tance in La-Ca-Mn-O ferromagnetic thin films. *J. Appl. Phys.*, 76(10):6929,
1994.


[47] W. Teizer, F. Hellman, and R. C. Dynes. Magnetic field induced insulator to
metal transition in amorphous-Gd$_x$Si$_{1-x}$. *Solid State Commun.*, 114(2):81,
2000.


[74] P. Xiong, B. L. Zink, S. I. Applebaum, F. Hellman, and R. C. Dynes. Low-


As discussed in R. Saito et al., Phys. Rev. Lett. 2, 27401 (2002), additional small peaks may be buried under the broad D and G peaks.


[114] Hua Wu and Matthias Scheffler, private communication.


