CHAPTER 2

MATERIALS FOR SEMICONDUCTOR SPIN ELECTRONICS

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DISCUSSION

A generic spin electronic device consists of a spin injection electrode, an interface, a medium in which coherent, polarized injected spins may be manipulated, and another interface beyond which the coherence and direction of the spins may be detected. Although spin injection and detection have been demonstrated by optical techniques (see Chapter 5) in order to produce an all electronic device, the ferromagnetic injector and detector must be materials having high spin polarization and compatibility with the transporting medium.

![Figure 2.1](image)

Figure 2.1. Generic semiconducting spintronic device with polarized electrodes.

Figure 2.1 shows such a generic spin electronic device, which includes a gate above the semiconducting transport medium for spin and charge manipulation. In the past, the ferromagnetic injector had been a ferromagnetic metal or alloy containing 3d transition elements with fractional spin polarization of the conduction electrons (Johnson and Silsbee 1987; Monzon and Roukes 1999; Gardelis et al. 1999; Hammar et al. 1999). However, as Schmidt et al. (2000) have argued, to get measurable spin polarization in the transport medium, the ratio of the conductivity of the injector $\sigma_{FM}$ to the conductivity of the transport medium (semiconductor) $\sigma_{SC}$ has to be smaller than or at least close to one, i.e. $\sigma_{FM}/\sigma_{SC} \approx 1$. This theoretical calculation neglects interface scattering, among other assumptions, but it does point toward the difficulties that arise when a magnetic metal is in contact with a nonmagnetic transport medium such as a semiconductor. A partial solution to the problem is either to produce the injection by tunneling spin-polarized electrons through an insulator into the semiconductor or by tunneling non-polarized electrons through a magnetic insulator spin filter (Hao, Moodera, and Meservey 1990; Fiederling et al. 1999; Jonker et al. 2000). A second, more practical, solution would be to start with a 100% polarized ferromagnetic injector. From the previous discussion, it is clear that the electrode materials necessary to produce a successful semiconductor spin electronic device require considerable materials and interface research. In this chapter,
the focus will be on the materials themselves. The next chapter by R. Buhrman will describe in detail the
vagaries of interfaces and their ability to help and/or hinder successful injection of spin-polarized carriers.

There have been numerous attempts to inject transition metals or their alloys into semiconductors, either
directly (Johnson and Silsbee 1987; Monzon and Roukes 1999; Gardelis et al. 1999; Hammar et al. 1999) and
also recently in a tunneling geometry (LaBella et al. 2001). The latter, using an Ni tip in a scanning
tunneling configuration, produces a remarkable ~92% spin-polarized current in GaAs. Major efforts to seek
additional solutions utilizing less conventional ferromagnets are currently in progress. These fall broadly
into the two categories that are discussed in the present chapter: (a) magnetic semiconductors and (b) half-
metals, many of which have the additional advantage that their magnetic transition temperatures exceed room
temperature, making them popular candidates for practical applications.

In this report, much of the discussion will focus on the concentrated magnetic semiconductors, such as the Eu
chalcogenides, EuX (X=0, S, Se, Te) (Methfessel and Mattis 1968; Wachtler 1972; Holtzberg, von Molnár
and Coey 1980). These materials, although they contain a magnetic species, the rare earth, at every lattice
site, have transition temperatures far below room temperature and thus are primarily suited for fundamental
studies and proof-of-concept type devices. On the other hand, much is known about their magnetic and
transport characteristics. Furthermore, the doped materials are 100% spin-polarized for low carrier
concentrations (von Molnár 1970; Santos et al. 2001; Steeneken et al. 2002). This also makes them favorable
from the point of view of the Schmidt (2000) argument, because the conductivity of this completely polarized
injector can be tuned to be comparable to that of the semiconductor transport medium. This report also
describes briefly the diluted magnetic semiconductors (DMS), which include both II-VI:Mn with transition
temperatures never higher than a few Kelvin (Haury et al. 1997), and the III-V:Mn DMS (Munekata et al.
1989) in which ferromagnetic transition temperatures as high as 110K have been confirmed (Matsukura et al.
1998) and where claims of transition temperatures in excess of 900K (Sonoda et al. 2002) have been
reported. Confirmation of these higher transition temperatures is pending. Other Mn-doped semiconductors
that are being reinvestigated as potential room temperature ferromagnetic spin sources are the chalcopyrites
such as CdGeP₂:Mn (Methfessel and Mattis 1968; Medvedkin et al. 2000; Mahadevan and Zunger 2002).
Several nontraditional DMS variants — among them TiO₂:Co (Masumoto et al. 2001; Shim et al. 2002) and
ZnO:Co (Ueda, Tabata, and Kawai 2001; Yang et al. 2002) — may also show promise. The class of DMS
also includes the mixed valence perovskites, which in some cases exhibit ferromagnetic order above room
temperature. These complex materials have been researched heavily over the past decade and will not be
summarized in this report, with the exception of some discussion on tunneling devices by James Daughton in
Chapter 6. The reader is directed to a review in 1996 by Coey et al., as well as a more recent review by
Ramírez (1997).

The discussion of half-metals will be limited to oxides including Fe₂O₃ (Penicaud et al. 1992) and CrO₂
(Watts et al. 2000), a brief description of Heusler alloys (Coey 2001), and several transition metal pnictides
including MnAs (Beam and Rodbell 1962), MnSb (Akinaga et al. 2000a), CrAs (Akinaga et al. 2000c), and
CrSb (Zhao et al. 2001). As a matter of orientation, it is useful to describe the difference between magnetic
semiconductors below their magnetic ordering temperature and the half-metallic ferromagnets by referring to
Figure 2.2 (Wolf et al. 2001), which gives a schematic density of electronic states for the two cases. The
principal observation, both in Figures 2.2a and 2.2b, is that only one of the two sub-bands is occupied, which
means that in both examples the electrons are expected to be completely spin-polarized. One should be
forewarned, however, that these are schematic densities of states, and as will be shown for the case of CrO₂,
the density of electronic states may be far more complicated than is indicated here. The splitting between the
two spin-polarized sub-bands may naively be thought of as the result of an effective Zeeman splitting of the
bands as indicated in Equation 2.1.
A concentrated magnetic semiconductor below $T_c$  

The half-metallic ferromagnet CrO$_2$

![Figure 2.2. Schematic density of states for EuS and CrO$_2$ (Wolf et al. 2001). Note that the energy scale is almost ten times larger in figure 2.2b.](image)

Equation 2.1

\[ E = \mu_0 \left( g^* \mu_B H + 2 J \langle \vec{S} \rangle \cdot \vec{s} \right) \]

Although a mean field approximation, this expression points towards several important physical results. The first term is the normal Zeeman term composed of the product of the effective “$g$” factor, $g^*$, the Bohr magneton, $\mu_B$, and the applied magnetic field strength, $H$. The second term represents the effective exchange interaction between the spin of the conduction electron, $\vec{s}$, with the average magnetization $\langle \vec{S} \rangle$ seen by the electron through its magnetic coupling strength, $J$. This second term is often orders of magnitude larger than the first; and $\langle \vec{S} \rangle$ may extend over the entire lattice, in which case it represents the magnetization dependence of the electron energy. This splitting is, for example, of order 0.5 eV in EuS (Methfessel and Mattis 1968; Wachter 1972). It may also represent the value of the spin, $\vec{S}$, averaged over the region occupied by an impurity electron. In this case, that second term may result in magnetic polaron formation, which is local ferromagnetic order in a paramagnetic or antiferromagnetic host (von Molnár 1970). These effective exchange interactions produce very large energy changes in the spin up and spin down band states, regardless of whether or not they are occupied. For example, figure 2.3 shows arguably the first spin electronic device (Esaki, Stiles, and von Molnár 1967), a metal/magnetic insulator/metal junction in which the thickness of the insulator was great enough (on order 10 nm) to prevent direct tunneling from one side to the other.
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Figure 2.3. Fowler-Nordheim tunneling. The bottom of the conduction band (--) is split in the presence of an applied field or below the magnetic ordering temperature, thereby facilitating an exponential increase in tunneling current as the effective tunneling distance decreases.

Large bias voltages, however, induce internal field emission (Fowler-Nordheim tunneling), which demonstrates that the field emission current depends directly on the state of magnetization of the insulator. This result provides direct evidence for the large band splitting found in Eu chalcogenides. The magnetic insulator thus serves as an efficient spin filter discriminating against spins in the opposite direction to the direction of magnetization of the insulating film. Other tunneling geometries utilizing doped conducting EuO as a spin source are being investigated. Work on the Eu chalcogenides has also demonstrated that the insulator (Holtzberg et al. 1964), when doped with carriers, enhances the exchange interaction, thereby increasing the magnetic ordering temperature with doping for low carrier concentration changes. This latter effect turns out to be very important for discussion of the DMS systems. Although II-VI DMS have provided important insight into spin injection as spin filters and spin transport media (Fiederling et al. 1999; Jonker et al. 2000; Kikkawa et al. 1997) that will be discussed in subsequent sections, their use as polarized spin sources is, for all practical purposes, unimportant for spin electronic semiconducting devices. The discussion of DMS in this chapter therefore will concentrate on the III-V materials. Recent successes by the Japanese groups headed by Ohno (Ohno 1998; Dietl, Ohno, and Matsukura 2001) and Munekata (Slupinski, Munekata, and Oiwa 2001) demonstrate that the versatility of DMS is still being explored. The definitive

Figure 2.4. III-V dilute magnetic semiconductors GaMnAs with $T_c$ as high as 110K for $X_{Mn}$ ~0.05 (reprinted by permission from Ohno 1999, © 1999 Elsevier).
recent work in the (Ga,Mn)As system (Ohno 1999) is summarized in Figure 2.4, which shows, in the left
hand panel, magnetic hysteresis measurements at 5K for a material containing 3.5 atomic percent Mn.
Similar curves can be obtained for concentrations ranging from approximately 1.5 to 7 atomic percent Mn as
indicated in the right hand panel. It is seen that the maximum value of the ferromagnetic transition
temperature $T_C$ is obtained at approximately 5%. These numbers, however, depend to a large extent also on
annealing conditions, as has been reported by Hayasaki et al. (2001) and Endo et al. (2001). Further impetus
to continue research in the DMS-type materials was given in several articles by Dietl, Ohno, and their
colleagues (Dietl et al. 2000) in which they predicted magnetic ordering temperatures in excess of room
temperature for five atomic percent Mn doping in GaN and ZnO. These predictions have resulted in major
U.S. efforts, centered at the University of California at Santa Barbara, Notre Dame University, the University
of Florida, and various programs in Japan. So far, the most spectacular result is that of Sonoda et al. (2002),
who produced data on (Ga,Mn)N of magnetization versus temperature up to approximately 750K. Utilizing a
Brillouin function extrapolation of their data, they found an estimated ferromagnetic ordering temperature,
$T_C$, at approximately 940K. Similar results have recently been reported by other laboratories (Thaler et al.
2002) including $T_C$s as high as 270K in GaP (Theodoropoulou et al. 2002). There is, therefore, high
probability that a single phase material can be produced and that transition temperatures will reach practical
values greater than room temperature. Observation of an anomalous Hall effect at room temperature would
provide confirmation that the nitrides and phosphides are indeed homogeneous ferromagnets.

Multiphase materials in which one of the components is magnetic with high transition temperature may turn
out to be useful, particularly in magneto-optical applications. It is generally believed, however, that single
phase materials will provide the best opportunities for effecting efficient spin injection into semiconductors.
Thus the new materials provided through combinatorial synthesis — initiated by Matsamoto et al. (2001),
which indicated ferromagnetism at room temperature for anatase type TiO$_2$:Co — caused great excitement.
The structural nature of the material is, however, still in question. For example, recent work by Chambers et
al. (2001) also shows large hysteresis at room temperature, both through magneto-optic and magnetic
measurements. The resulting magnetization per Co dopant varies widely with preparation, however, which
suggests that perhaps either elemental Co or an unknown Co-Ti-O compound have been produced within the
anatase matrix. Additional studies also support the contention that the material is multiphase (Kennedy and
Stampe 2002). Clearly, considerable research must yet be done to determine the physical and chemical
properties of these DMS systems. It should be noted that the initial work on the (Ga,Mn)As also evidenced
multiphase structures in which the Mn combined with As to form the ferromagnet MnAs with a
ferromagnetic $T_C$ approximately equal to 300K. Only after considerable experimentation was it possible to
make these materials as demonstrable homogenous DMS (Munekata et al. 1989).

Nonetheless, a number of fascinating new discoveries in multiphase and novel nonequilibrium magnetic
pnictides have been made. The first of these is the deposition and burial of 3 nm islands of MnSb in a GaAs
matrix. This material has been shown to have enormous low field magnetoresistive properties. Akinaga et
al. (2000b) report a room temperature magnetoresistance ratio reaching 880% at .1 T and 320,000% at .2 T.
These authors were also able to explore hysteretic switching behavior at various bias fields. Clearly such
effects should find utility in various magnetoresistive switch applications. Other examples are reports of
unstable zinc blend forms of CrAs (Akinaga et al. 2000c) and CrSb (Zhao et al. 2001) that have been
successfully prepared by ultrathin film deposition onto GaAs substrates. These materials are room
temperature ferromagnets that are predicted to be completely spin-polarized. Clearly there is great potential
for these metastable magnetic metal pnictides, since they may serve as excellent spin sources grown
epitaxially onto technologically important semiconducting substrates.

Although the above mentioned pnictides appear to be half-metals, there is also considerable interest in other
better known half-metallic materials such as Fe$_3$O$_4$ (magnetite), CrO$_2$, and the family of Heusler alloys.
Magnetite, although it is not a diffusive but a hopping conductor, both above and below a structural phase
transition called the Verwey transition ($T_v \sim 120K$), is a ferrimagnet with a transition temperature of 865K
(Mott 1990). A ferrimagnet is a material in which the magnetic ions are coupled anti-ferromagnetically
where the two sub-species of magnetic ions have different moments such that there is a net magnetization
upon ordering. Recent experiments pioneered by Coey et al. (Versluijs, Bari, and Coey 2001) in Ireland have
shown that small-area point contacts can yield enormous magnetoresistive effects. Their initial results,
defined by the inverse slope of the I-V characteristic at 0 bias voltage, demonstrate a remarkable negative magnetoresistance. Furthermore, the curves are hysteretic, making it possible to use these materials as memory elements and switches. The effects are very large, and although these initial results indicate the potential, they were made on break junctions of single crystal material. The possibility of structuring single crystal films of magnetite and performing nanofabrication patterns on them should lead to highly controlled room temperature giant negative magnetoresistive devices.

In principle, the Heusler alloys for which the term “half-metals” was originally coined would appear to be a tantalizing materials system. They suffer, however, from the fact that their materials properties can vary widely unless these complex three component materials are produced stoichemetrically. The formula is ordinarily Ni\textsubscript{2}MnX (X=Ga,Ge,In). Of these only the Ga material shows a well defined transition temperature above room temperature and a well defined hysteresis (Dong, Chen, and Palmstrom 1999). The others exhibit nonclassical magnetization behavior as a function of temperature and cannot simply be described by well established models. Furthermore, it is very difficult to produce thin films of these on semiconductors of technological significance. A notable exception is NiMnSb with a T\textsubscript{C} ~730K, which has been studied in the tunneling geometry (Tanaka et al. 1999). Research needs to be continued, and it is expected that developments in the United States, Europe, and Asia will lead to some breakthroughs in this materials system.

CrO\textsubscript{2} has been a source of great interest for possible spintronics applications ever since it was discovered through Andreev reflection measurements that this material, at least at low temperatures, is essentially 100% spin-polarized (Soulen et al. 1998). This is the only binary oxide that is both a ferromagnet and a metal. Although it is widely used in recording applications, until recently there was little known about its electronic structures, although various band structure calculations indicate that it is half-metallic (Schwarz 1986). CrO\textsubscript{2} crystallizes in the rutile structure, has a ferromagnetic transition temperature of 400K, and an integral magnetic moment of 2\textmu\textsubscript{B} per Cr ion. The material is difficult to produce in single crystal form epitaxially onto any substrate other than rutile (Chamberland 1977), although textured materials can be grown onto sapphire (Ishibashi et al. 1978). There are no reports of CrO\textsubscript{2} ever having been produced in textured or epitaxial thin film form onto GaAs or Si. Furthermore, magnetotransport properties of this material are complex (Watts et al. 2000). The Hall resistivity, as a function of magnetic field, does not behave like a ferromagnetic metal, for temperatures between that of liquid He and 100K, but rather shows a crossover as a function of field indicative of both hole and electron contributions. The data are most easily analyzed in terms of a two-band approximation. In the spirit of this type of analysis, one finds that there are both highly mobile holes moving in concert with more numerous but less mobile electrons (Watts et al. 2000). Thus the band structure is somewhat more complex than initially assumed. However, all transport data examining the spin polarization, which includes various forms of analysis of Andreev reflection data (Ji et al. 2001; Parker et al. 2002) as well as Tedrow-Meservey type tunneling spectroscopy (Parker et al. 2002), strongly support the contention that the carriers are completely spin-polarized at low temperatures in this material. There is also evidence from spin-polarized photoemission that 80% of the polarization exists even at room temperature. Suffice it to say that the existence of highly spin-polarized carriers at room temperature and above has to be confirmed in an all electronic device structure before CrO\textsubscript{2} becomes a candidate for spin sources or detectors for application.

CONCLUSIONS

This review of materials activities in spin electronics for semiconductors applications has demonstrated that much of the new materials effort is driven by Japan’s innovation. In the opinion of the WTEC panelists, this dominance may be traced back to Japan’s recent history of leadership in materials development in, for example, the mixed valence perovskites. It is not an overstatement to suggest that much of the fundamental work on single crystals of manganese and high T\textsubscript{C} materials was performed on single crystals emanating from Tokura’s group in Japan. Furthermore, the government of Japan made an early decision to fund the project “Spin Controlled Semiconductor Nanostructures” in 1996 with an award in excess of $6,000,000. This program, led by Professor H. Ohno, Tohoku University, was a great success and pulled together a large number of the practitioners of materials research in transition metal and rare earth compounds and alloys.
Finally, and this cannot be emphasized too strongly, there exists a strong synergistic effort between theory and experiment. A very good example of this synergy is the large scale computational effort of the group of Katayama-Yoshida and the response by many groups, including that led by Koinuma, using combinatorial synthesis to attempt to find the predicted properties. Although the United States has recognized that materials research is going to be a vital component of any successful new spin electronics semiconductor technology, and there are a number of excellent efforts in semiconductor spintronics, the support for this work has been primarily championed by DARPA. A broader program involving other government funding agencies will be necessary to compete favorably in the area of materials synthesis and fabrication. It is, therefore, noteworthy that the NSF announced, in November 2001, a new initiative entitled “Spin Electronics for the 21st Century.”

REFERENCES

2. Materials for Semiconductor Spin Electronics


Parker, J.S. et al. 2002. Submitted for publication.


