Spin-Valve Behavior in Aligned Arrays of Carbon Nanotubes

DISSERTATION

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By

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Abstract

We report the operation of spin-valve structures formed from aligned arrays of multi-walled carbon nanotubes up to 10 μm in length. The devices require only one additional ferromagnetic layer with the ferromagnetic catalyst nanoparticles of either iron or cobalt serving as the other magnetic electrode. Peaks in the resistance occur clearly as a result of the reversal of the magnetization of the electrodes. Several variations of this structure are examined: spin-valve structures formed from arrays of aligned carbon nanotubes with internal iron catalyst nanoparticles, a protective SiO₂ cover layer, and directly-deposited iron films; arrays grown and embedded in porous anodized aluminum oxide, incorporating cobalt nanoparticles and directly-deposited iron films; and spin-valves constructed from nearly-fully-spin-polarized films of La₂/3Sr₁/3MnO₃ (LSMO) and containing iron nanoparticles. We have observed spin-dependant transport in these devices with maximum observed magnetoresistances ranging from 1.5% for aluminum oxide grown devices to in excess of 30% in LSMO-based devices. Spin diffusion lengths in these multi-walled carbon nanotube arrays are calculated to be at least 15.6 μm.
For Sarah
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Chapter 1: Introduction

Traditional electronics rely on the manipulation of currents of charged electrons to convey motive means or, especially, information through a system. The sign and magnitude of this charge current are a tunable degree of freedom to that allows simple operations. By making use of the intrinsic quantum angular momentum, the spin, of the electrons, a second degree of freedom is available to perform more complex operations. The realization of this idea is the foundation of the young field of spintronics (a portmanteau of Spin Transport Electronics), wherein manipulation of the direction of the spin of charge carriers, either along with charge or in a spin-only configuration (a spin-current) allows construction of magnetic field sensors, stable information storage, zero-current conveyance of information, and the potential for quantum computational operations. In most bulk matter, populations of spin species are in equilibrium, and therefore charge currents flowing through them will likewise be randomized into an equilibrium state. When a current flows through a material that has an excess of one spin species, it gives the current a preponderance of one species and that information is conveyed until such time as the current has scattered this net spin direction back to equilibrium. By cleverly choosing materials to both produce and transmit this current that is dominated by one spin species it has become possible to transmit this information, encoded in the net spin direction of the current, across nearly-macroscopic distances (tens of microns at present).
We present here the production and measurement of devices whose resistance is sensitive to the presence of external magnetic fields, so-called spin-valves, constructed from aligned arrays of carbon nanotubes and making use of several materials to achieve currents with a net spin direction.

The mechanisms by which nanotubes provide excellent spin transport and are thus useful in a spin-valve configuration have their origin in the details of charge transport in nanotubes which in turn is directly dependent on the physical structure of nanotubes. Therefore we start with structure and electronic details of carbon nanotubes in Chapter 2. In order to arrive at the carbon nanotubes with a current containing spin information, we must first polarize the current with a spin-polarized material and transmit it successfully across the interface to the nanotube. The origin of spin-polarization and the mechanisms that allow or confound the transmission of this information to or through carbon nanotubes is described in Chapter 3. Lab methods for fabrication, measurement, and validation and verification of spin-valve devices, as well as data analysis are detailed in Chapter 4. Chapter 5 presents evidence for hysteretic magnetoresistance indicative of the spin-valve effect in systems constructed from traditional ferromagnetic (Fe) films, aligned arrays of multi-walled carbon nanotubes, and ferromagnetic nanoparticles that also serve as growth catalysts for the nanotubes. Both SiO$_2$-protected and AlO$_x$-encapsulated arrays are utilized, achieving magnetoresistances of -15% and +1.5%, respectively. Chapter 6 describes devices that utilize the highly spin-polarized manganite, La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO). This material has the advantage of a higher maximum polarization in transmitted current, and we describe spin-valves that exhibit
magnetoresistance in excess of -30%, indicating a very long spin diffusion length in multi-walled carbon nanotube arrays of at least 15.6 um. Unusual positive magnetoresistance effects observed during relaxation of applied magnetic field (rather than after a switch in field direction) are also examined. Chapter 7 provided conclusions drawn from these various methods and materials and thoughts on which spin-valve devices and measurements of spin transport through carbon nanotubes might be expanded and improved upon by further work. A brief discussion of other future directions of interest concludes.
Chapter 2: Background on Carbon Nanotubes: Structure and Charge Transport

2.1 Structure of Carbon Nanotubes

Single-walled carbon nanotubes (SWNT) have the form of a sheet of graphene—a single plane of graphite—that has been rolled to form a tube [Figure 1]. Vectors $a_1$ and $a_2$ define the hexagonal lattice of graphene, with each unit cell containing two carbon atoms. Many properties of CNT depend on the size and relative twist, or chirality of the CNT. For CNT rolled from this lattice, the chiral vector $C_h$ defines the circumference of the CNT and can be described in a discrete number of steps of $a_1$ and $a_2$, such that $C_h = n a_1 + m a_2$, where $n$ and $m$ are integers.

Figure 1: (left) Wrapping of a 2D graphene sheet to form a SWNT, showing lattice vectors $a_1$ and $a_2$, the chiral vector $C_h$, and the chiral angle $\theta$. (right) Resulting (5,3) SWNT from a chiral vector moving 5 steps along $a_1$ and 3 steps along $a_2$. Copyright Royal Society of London, 2004; reprinted with permission.¹
Figure 2: Diagram of lattice vectors $a_1$ and $a_2$, along the graphene sheet and resulting (n,m) indices which give the chiral vector, $C_h$. The translational vector $T$ points up along the dotted line from the origin. Copyright Physical Society of Japan, 2005; reprinted with permission.\(^2\)

Likewise, a translational vector $T$ [Figure 2] is defined such that

$$T = \frac{2m+n}{d_R} - \frac{m+2n}{d_R}, \text{ } d_R \text{ greatest common divisor of } 2m+n, m+2n \quad (1)$$

The rectangle defined by $C_h$ and $T$ is the unit cell of the CNT, containing $N$ (hexagonal) unit cells of graphene and $2N$ carbon atoms.\(^3\)

$$N = 2 \frac{n^2+m^2+mn}{d_R} \quad (2)$$

To give direction along the lattice, a chiral angle $\theta$ is defined between $C_h$ and $a_1$. Due to symmetry of the hexagonal lattice, it is only necessary that $\theta$ vary over $30^\circ$ (larger angles
can be mapped to 0-30°). The indices \( n,m \) are used to give the relative size and chirality of a CNT, for instance \((5,5)\) indicates a CNT where a circumference is formed by traveling five steps along both \( a_1 \) and \( a_2 \), giving a chiral angle of \( \theta=30° \). Thus \((n,m)\) can vary from \((n,0)\), called “zigzag” to \((n,n)\), called “armchair”. All other \((n,m)\) are generically called “chiral” (or more precisely, armchair and zigzag CNT are achiral because they have a higher symmetry). Observed SWNT range in diameter \(0.4\) nm\(^1\)\(^3\) to at least \(10\) nm,\(^3\) and have been grown to lengths of several centimeters.\(^4\) The individual layers of MWNT can be described in the same way and MWNT take the form of concentric SWNT wrapped around each other in a tree-ring pattern. The spacing between layers of MWNT is \(\sim 0.34\) nm,\(^5\) essentially the same as for graphite or multi-layered graphene.\(^1\)\(^3\) Observed MWNT range from less than \(1.4\) nm\(^6\) to at least \(100\) nm\(^5\) in diameter and have also been grown to lengths of several centimeters.

In graphene, the \(2p_x, 2p_y,\) and \(2s\) orbitals of each carbon atom are \(\sigma\)-bonded to the nearest neighbor atoms, and these undergo \(sp^2\) hybridization, giving the characteristic flat honeycomb. The electrons in the fourth \((2p_z)\) orbitals form covalent \(\pi\) bonds. With each carbon contributing one \(\pi\) electron and with two carbon atoms per cell, the \(\pi\) bands are completely occupied (highest occupied molecular orbital) and conduction must be through the empty anti-bonding \(\pi^*\) band (lowest unoccupied molecular orbital). Using a tight-binding model,\(^1\)\(^3\) we look at the first Brillouin zone for graphene [Figure 3] and we see that at \(K\), the corners of the zone, \(\pi\) and \(\pi^*\) are degenerate at the Fermi energy. This is because of symmetry requirements: the two carbon atoms of the unit cell are
indistinguishable and must be equivalent. Therefore, graphene is a zero-gap semiconductor with conduction through the degenerate $\pi/\pi^*$ orbitals of the 2D sheet.

Figure 3: Energy dispersion relation for the first Brillouin zone of 2D graphene, with high symmetry points marked. (inset) a cross section of the 2D zone, showing one possible 1D dispersion relation through the high symmetry points. Notice zero band gap at points $K$. Copyright Imperial College Press, 1998; reprinted with permission. \(^3\)

When the graphene layer is rolled into a CNT, two important alterations in the physical and band structure occur. First, all directions are no longer equivalent- there are now wave vectors $k_x$ parallel to the chiral vector $C_h$ (along the rolling circumference) and $k_y$ parallel to the translational vector $T$ (along the axis). With finite circumference and necessary boundary conditions (the wavefunction must match where the edges join- $\psi(r + C_h) = \psi(r)$), $k_x$ now has discrete values $k_x = \frac{2\pi g}{|C_h|}$, with integer $g$. \(^2\) The axial $k_y$ remains continuous for relatively long NT lengths (but is also discrete for very
short CNT- this has been observed experimentally).\textsuperscript{3} Thus, SWNT represent a quasi-1D structure.\textsuperscript{4} The energy dispersion for 1D CNT resembles a cross-section of the 2D dispersion that exists for graphene. One possible cross-section is shown in the inset of Figure 3, wherein the slice passes through the point $K$. However, $C_h$ and $T$ are distinguishable directions in 1D CNT ($a_1$ and $a_2$ in 2D graphene are not), therefore we observe two inequivalent points, $K$ and $K'$ at the corners of the Brillouin zone of the NT. There are $N$ such 1D energy bands in the first Brillouin zone (again, one electron for each carbon atom, two electrons per band), with $N$ as given above [Equation 2].

When bands cross at the $K$ points of the Brillouin zone of the NT (can also be worked out for $K'$), there is no band gap, and the CNT is metallic. We draw the wave vector $k_x$ in the Brillouin zone. In order for a band to cross $K$, the vector from $k_x$ to $K$ must have a length that is a multiple of $k_y$- that is, we must be able to go from our starting point to $K$ in a discrete number of wave vectors $k_y$. This occurs when

$$\overline{YK} = \frac{2n+m}{3} k_y$$

where $Y$ is the nearest point to $K$ on $k_x$. This can be said simply: we can define two integers $j$ and $M$, such that $n - m = 3M + j$.\textsuperscript{2} When $j = 0$, the CNT has no bad gap and thus has metallic behavior. Armchair $(n, n)$ nanotubes are thus always metallic, as are one third of all CNT chiralities. The remainder have $j = \pm 1$, have non-zero band gap, and are thus semiconductors [Figure 4].
The second effect of joining the graphene sheet to form CNT is that there is now curvature to the lattice and this leads to Peierls distortion and a small band gap of order meV. This band gap decreases with increasing diameter (which implies lower curvature), scaling like $1/d$ in semiconducting CNT and $1/d^2$ in non-armchair metallic CNT. Very large diameter CNT have sufficiently small curvature that they reach a state approximating graphene (i.e. they look locally flat and have [almost] no band gap). For high curvature, the $\pi$-band-only band-folding picture of the tight-binding model becomes less accurate, and it has been shown by other models (local density functional calculations, tight-binding model with all four valence electrons), that the band gap decreases for NT with very small diameters ($\lesssim 0.7$ nm) due to hybridization of the $\sigma^*$ and $\pi^*$ bands, such that CNT on the order of 0.4 nm become metallic despite the Peierls
distortion. This has also been put forward as an explanation for observed superconductivity in 0.4 nm CNT, though this is not well agreed upon as an explanation.

For non-armchair metallic CNT, the small band gap caused by curvature will only be noticed at very low temperatures such that $E_{\text{gap}} \sim meV \geq k_BT$ and thermal fluctuation no longer cause conduction across the gap. Thus, for easily obtainable temperatures, all metallic (by index) CNT will continue to act metallic. The band gap in all semiconducting nanotubes becomes smaller as tube radius increases (as it approaches the form of graphene), and thus all nanotubes of large radius above $\sim 15 \text{ nm}^5$ can be considered metallic at room temperature as the band gap is smaller than $k_BT = 0.0258 \text{ eV}$, $T = 300 \text{ K}$ and thermal fluctuations will allow conduction (this is mostly relevant in MWNT, which are frequently above this size- see Section 2.2.4).

2.2 Charge Transport in Carbon Nanotubes

2.2.1 Classical Transport

In macroscopic objects, we make a number of sensible approximations concerning charge transport. We treat electrons as particle-like with no phase or momentum coherence, and without regard for wave-like interference between electrons. We assume resistivity, $\rho$, and conductivity, $\sigma$, are constants for a given material, independent of size. This picture accurately describes movement of charge in large scale objects with low mean free paths $L_\phi < L_m \ll L$, where $L_m$ is the mean free path between scattering events, $L_\phi$ is the mean phase coherence length, and $L$ is the length of the conduction channel$^3$ such that we can expect all charge carriers to scatter many times
over the length of object and can expect all wave phase coherence to be lost between each scattering event. In this case, we that find the resistance of a wire is

\[ R = R_c + NR_0 \frac{1-T}{T} \]  

(4)

where \( R_c \) is the contact resistance of the wire, \( N \) is the number of scattering events \( N = \frac{L}{l_m} \), \( R_0 \) is the quantized unit of resistance (explained below) and \( T \) is the transmission probability for a single scattering event (note that by definition, \( \frac{(1-T)}{T} = 1 \) for the mean free path [50% transmission]). This means that the resistance scales directly with length as charge carriers scatter many times, which is to say that resistance conforms to Ohm's law \( R = \rho \frac{L}{A} \) for bulk metals which is, of course, what we expect.

### 2.2.2 Ballistic Transport in SWNT

As mentioned previously, CNT (in particular SWNT) represent a quasi-1D system.\(^4\) They can be described as a quantum wire,\(^3\)\(^,\)\(^8\) in which the molecular wavefunctions are discrete around the circumference of the CNT and may extend the whole length of the CNT and therefore have discrete channels of conduction. In such a case, conduction in the CNT is said to be ballistic, meaning that the charge carriers can, on average, travel coherently for distances longer than the length of the channel (i.e. the portion of the CNT through which the transport is occurring) without momentum or phase relaxation: \( L_m > L_\varphi > L \).

For a 1-D wire with chemical potentials \( \mu_1 \) and \( \mu_2 \) at its two contacts and \( M \) conduction channels, current flowing through the wire is given by
where \( V = \frac{\mu_1 - \mu_2}{e} \) is the bias across the wire, and the ballistic resistance across the wire is

\[
R_c = \frac{(\mu_1 - \mu_2)e}{I} = \frac{h}{2e^2 M} \frac{1}{l}
\]

This is the contact resistance of the wire, with no resistance along the length of the wire. This resistance scales inversely with the number of conduction channels, so for single-channel conduction, we can define \( R = R_0 = \frac{h}{2e^2} \) as a single unit of resistance, where \( R_0 = 12.9 \text{ kΩ} \). It has been pointed out\(^4, 6, 9\) that this channel still includes spin degeneracy, so we should have \( \frac{1}{2} R_0 = 6.5 \text{ kΩ} \) as our true quantum of resistance, with the quantum of conductance \( G_0 = \frac{1}{R_0} \).

In fully ballistic conduction (i.e. for \( L \) at least a factor of several less than \( L_m \)), SWNT approach this quantum of conductance \( G_0 = 4e^2/h \), thus giving a maximum current through each SWNT of ~25 μA at a reference bias of 1 V.\(^{10}\) Ballistic transport has been observed first in many metallic SWNT systems,\(^1-3\) and has also been seen in semiconducting SWNT where good contact is made to the electrodes, with mean free paths reported on the order of several hundred nm\(^9\) to several μm.\(^{10}\)
<table>
<thead>
<tr>
<th>Regime</th>
<th>Relationship</th>
<th>Coherence length</th>
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<tbody>
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<tr>
<td>Strong</td>
<td>$L_m &gt; L_m$</td>
<td>$L_c$</td>
</tr>
</tbody>
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Table 1. Transport regimes of a conductor, showing the length regions in which ballistic, classical, and diffusive (localized) transport are in effect. Defect-free CNT of moderate length are ballistic conductors with mean free path $L_m$ of hundreds of nm to several μm. After Saito.\(^3\)

2.2.3 Diffusive Transport in SWNT

In diffusive transport, the mean free path is much smaller than either the channel length or the phase length $L_m < L_m < L$ such that many scattering events occur over the length of the channel, but phase coherence is maintained for longer than the mean free time. This leads to multiple coherent reflections off of scatters, and this state is also known as localization. The chances of traveling the large channel length $L$ without reflecting are very small and the resistance of the wire does not scale linearly with length:

$$R(L) = \frac{R_0}{2} \left[ e^{\frac{2L}{L_c}} - 1 \right] \to \infty, L \to \infty$$

(8)

where $L_c$ is the localization length. This kind of localization depends on the interaction of the electron wavefunction with a random potential and is called Anderson localization. Localization from electron-electron repulsion upon reaching a critical carrier density, large compared to the level spacing, creates a 'traffic jam'- this is called Mott localization.\(^3\)
Despite a loss of ballistic conduction, the diffusive transport still differs from classical transport in which phase coherence is lost between scattering events, and multiple reflections are unlikely [Table 1].

Resistance scales linearly with length via Ohm's law in classical transport, where it does not in diffusive transport. Diffusive transport is seen in very long CNT and CNT with many defects. In this case, the defects create barrier 'islands' between otherwise ballistic regions and electrons are localized to each island and must tunnel to the next ballistic region.

2.2.4 Transport in MWNT

Drawing from the understanding of SWNT, we can develop a picture of transport in multi-walled nanotubes. MWNT are composed of anywhere from two to potentially hundreds of concentric graphene sheets, where many or all of these shells are of greater diameter than that of most SWNT (cf. Section 2.1). MWNT are essentially always metallic when considered as a whole because some of their multiple walls will be metallic (some semiconducting). In addition, as mentioned above the large diameter of these walls (in MWNT) will tend to make even the semiconducting walls metallic at room temperature. One problem that MWNT present is in making a good contact to them with device electrodes by way of traditional lithography. Often only the outermost wall is (or few walls are) electrically connected, resulting in much lower conductance than might be expected. Li reported growing a single MWNT from the tip of a tungsten filament, and then contacting the far end of the MWNT with another tungsten tip.
Figure 5] with a low applied voltage between tube and tip creating a weld for and a “perfect” Ohmic contact to [likely] all walls of the MWNT on both ends. They measure the conductance of the MWNT to be $\sim 450 \, G_0$, attributing this large conductance to participation of many or all of the walls and to interactions between the closely spaced walls and sub-bands formed as a result. This total number of conduction channels is described by

$$N = \sum_j^{N_{\text{wall}}} \sum_i^{N_{\text{subb}}} \frac{1}{e^{[E_{\text{occ}} - E_f]/k_B T} + 1}$$

where $N_{\text{wall}}$ and $N_{\text{subb}}$ the number of walls and sub-bands per wall, $E_{\text{occ}}$ is the highest occupied energy of the sub-band $i$, and $E_f$ is the Fermi energy. This multi-band, multi-channel ballistic conduction allows much larger currents per MWNT ($\sim 7 \, mA$ here) [Figure 6].
Figure 5: Scanning electron microscope image of a single MWNT attached to a movable probe tip and a conducting substrate, nanotube radius ~100 nm. The drawing indicates how I-V measurement was made of this device. Copyright 2005, American Physical Society; reprinted with permission.

Figure 6: (left) I-V measurements of single MWNT, made at room temperature, showing very high current through nanotube. (right) Conductance of nanotube, in units of $G_0$, with perfect conductance in a metallic SWNT being $2G_0$. Copyright 2005, American Physical Society; reprinted with permission.
Chapter 3: Background on Spin Transport

When spin information is conveyed from one place to another, there is said to be spin transport, in analogy to the conveyance of charge information in charge transport. Spin transport is most easily determined by means of the spin polarize/spin analyze method. Ferromagnetic materials, with the direction of their magnetization given by an excess of spins in one particular direction, are said to be spin polarized. In the simplest picture, the magnetization causes a shifting in the energy levels for spin-up and spin-down charge carriers [Figure 7, shown with a CNT spacer], with only the spin-direction aligned with the magnetization available at the Fermi level for conduction. As the conduction band states exist only for electrons with spin in this direction, the ferromagnet gives a similar predominance of spin direction to current flowing through it. The current is spin-polarized in analogy to the passage of photons through a polarized light filter (the analogy is inexact in that the incoming photons with the wrong polarization are absorbed or reflected, whereas incoming electrons with the anti-aligned spin direction are scattered or flipped, but return to the ferromagnet again and continue in the current due to the applied bias). This current, with a net spin polarization, then traverses an intermediary nonmagnetic (NM) layer before arriving at a second ferromagnetic layer. The specifics of this layer are examined below.
Figure 7: Schematic of the spin-valve effect emphasizing injection and detection of spin-polarized current that passes from the first ferromagnetic contact (F1) through a semiconductor (CNT) and into the second ferromagnet (F2). In (a) parallel alignment of the magnetizations of the magnetic contacts leads to a low resistance state. In (b) antiparallel alignment leads to a high resistance state. Figure courtesy J. D. Bergeson.

The second ferromagnetic layer also has a net alignment of its component spins, and the ease with which the electrons enter and pass through this ferromagnetic layer is determined by the interaction of the spin polarized electrons and the magnetization of the ferromagnet in much the same way as the first- conduction band states are available only to one spin species and electrons with a different spin directions will scatter from the interface [Figure 7]. Assuming that the spin information imparted to the electrons by the first FM is still present upon reaching the second FM, the effective resistance of the
device will be determined by the relative alignment of the two FM layers. If the layers are co-aligned, the spin current will match both FM and resistance will be low. If the FM layers are anti-aligned, the spin current will be in the direction of the first FM and will therefore scatter from the second with its opposite-spin available conduction band.

This simple picture is complicated in two obvious ways: the nature of transport through the spacing material (spin information is lost) and the extent of the polarization of the FM layers (polarization in not full). Numerous more subtle effects also play a role in effective spin transport.

### 3.1 Spin Transport in Nonmagnetic Material

The spacing layer between the FM layers can be insulating, in which case the mechanism is tunneling and the resulting variable resistance is called Tunneling Magnetoresistance (TMR). In TMR, the portion of the spin current that tunnels from the first FM to the second will have the same spin alignment throughout the spacing layer. Positive TMR in this FM/NM/FM arrangement has been described by Julliére’s model,\(^\text{12}\) giving the difference between the resistance (\(\Delta R\)) of the parallel \((R_p)\) and antiparallel \((R_{ap})\) alignments of the FM layers as

\[
\frac{\Delta R}{R_p} = \frac{(R_{ap} - R_p)}{R_p} = \frac{2P_1P_2}{1 + P_1P_2}
\]

where \(P_1\) and \(P_2\) are the spin polarization of the injecting and analyzing FM layers, respectively.

For semiconducting and conducting NM spacing layers, a more complicated model including the decay of spin information during transport is needed. After spin-
polarized current transits the tunnel junction from FM to NM as described above, it transits this spacing layer and the spin-polarization decays due to spin scattering mechanisms with a characteristic spin diffusion length, \( \ell_s \). We modify Jullière’s TMR model with a simple exponential decay term, \( e^{-\ell/\ell_s} \), for spin polarization loss along the length, \( \ell \), of the nonmagnetic channel\(^{13}\) (here, the MWNT array).

\[
\frac{\Delta R}{R_p} = \frac{(R_{ap} - R_p)}{R_p} = \frac{\pm 2P_1P_2}{1 + P_1P_2} e^{-\ell/\ell_s}
\] (11)

However, in many systems such as some of those described here, observed MR is negative, with the parallel resistance higher than the antiparallel state. This inversion of sign is in conflict with a simple understanding of Julliére’s model, but has been observed in a wide variety of magnetoresistive systems, often oscillating in sign with environmental conditions, especially an applied electric field from a back gate\(^{14-18}\) and several models have been proposed to explain this.\(^{19-22}\) As the devices used in these experiments consist of a multitude of parallel pathways, those models depending on local domain details at a given FM/MWNT interface or resonance conditions of an individual nanotube\(^{22}\) are unlikely to be able to explain the overall behavior of these devices. Instead we apply the somewhat simpler model that has been used to describe a wide variety of negative MR configurations: in the multitude of local domains (especially in the Fe nanoparticles), some are aligned and some anti-aligned with the bulk magnetization, dictated by edge effects, solid phase variation, and local domain size. Those local FM/NM/FM conditions with the lowest resulting resistance will be those represented in the measured device resistance and are analogous to the "best" devices in a batch of single-CNT devices. In keeping with the conventions of positive MR and
Julliére’s model, the resistance difference between the parallel and antiparallel states can be analyzed by assigning a leading negative sign as in Equation 11 above.

3.2 \( \text{LSMO} \)

In pursuit of better spin injection, a very high spin polarization in the contacting material has two important effects. Firstly, a current with a higher spin polarization on injection will have a correspondingly higher spin polarization upon reaching the \textit{analyzer} contact (or alternately will require a greater number of spin diffusion lengths to reach the same polarization at the \textit{analyzer} ferromagnetic contact). Secondly, injecting a nearly-fully-spin-polarized current has been suggested and demonstrated as a means of overcoming interfacial scattering systems where there is a conductivity mismatch between metallic ferromagnetic contacts and semiconducting transport material.\textsuperscript{23, 24} In the case of metallic MWNT, it is primarily the former that we are concerned with.

In the early 1990’s the first reports were made of a (nearly) fully-spin-polarized semiconducting manganite perovskite, \( \text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3 \) (LSMO) and related materials.\textsuperscript{25-28} This material appeared to have a \textit{half-metallic} band structure, meaning that conduction band states are available to only the majority spin carrier, leading to 100% spin polarization in the half metal and in currents transiting the half metal (in theory). The observed polarization on the surface of the LSMO, measured by several means approaches 100%, but likely contain some small portion of minority spin carriers.\textsuperscript{29} There is a strong dependence on surface and granularity effects,\textsuperscript{30} leading to lower observed spin-injection fractions into transport media, and for this reason, we give spin
diffusion length calculations for both the maximal ~95% polarization and a more commonly observed ~80%.\textsuperscript{31}
Chapter 4: Experimental Techniques

4.1 Sample preparation

4.1.1 Growth of Vertically Aligned Carbon Nanotube Arrays

Carbon nanotubes can be grown by several methods, including laser ablation, flame synthesis, carbon arc discharge, and chemical vapor deposition (CVD).\(^3\),\(^32\) When grown using this last technique, CNT can be grown in several conformations and in small numbers or in bulk. In the work presented here, CNT are grown in a densely-packed vertically aligned array at the University of Dayton.\(^33\)-\(^35\) The vertically aligned multi-walled carbon nanotubes are prepared by pyrolysis of iron (II) phthalocyanine (FePc) under Ar/H\(_2\) atmosphere at a predetermined temperature 800-1100 °C\(^33\),\(^35\)-\(^37\) using a Si substrate in a flow reactor consisting of a quartz glass tube and a dual furnace fitted with independent temperature controllers. In a typical experiment, the quartz substrate is about 10–20 cm apart from the FePc source [Figure 8]. The main specimens used for this study are prepared as follows: 0.3 g FePc is placed in one furnace and a clean SiO\(_2\)-coated Si wafer segment (ultrasonicated in acetone) is placed in the second furnace in the quartz glass reactor. A flow of Ar/H\(_2\) (1:1 by volume, 60–70 cm\(^3\)/min) is then introduced into the quartz tube while heating up the second furnace. Once the second furnace reaches a predetermined temperature of 850 °C, the first furnace is heated at 650–750 °C for ~10 min. Thereafter, both furnaces are kept at the pyrolysis temperature (850 °C) for ~10 min to complete the pyrolysis process. The resulting array is densely
packed, of a uniform length of 10 μm [Figure 9], and highly vertically aligned with Fe nanoparticles at both ends of MWNT as growth catalysts. A thick (~1 μm) layer of Cu is deposited on the top of the array and it is removed from the growth substrate, separating the MWNT from the Fe catalyst nanoparticles on the Si surface, leaving free-ended MWNT, as verified by scanning electron microscopy at Ohio State University. The diameter of the MWNT-encapsulated iron nanoparticles is dictated by the diameter of the nanotubes,\(^{36}\) in this case 50-100 nm [Figure 10].

Figure 8: Apparatus for the generation of aligned carbon nanotubes by pyrolysis of FePc. In typical experiments, a predetermined amount of FePc (0.1-0.3 g) and a clean quartz glass plate (4 x 1 x 0.125 cm, ultrasonicated in acetone) were placed in the quartz glass tube (as shown). A flow of Ar/H\(_2\) (1:1 to 1:2 v/v, 20-40 cm\(^3\)/min) mixture was then introduced into the quartz tube during heating. After the second furnace reached 800-1100 °C, the first furnace was heated to 500-600 °C for 2-15 min. Thereafter, both furnaces were kept at the pyrolysis temperature (800-1100 °C) for an additional 20-30 min for the deposition of nanotubes to be completed. Copyright 1999, American Chemical Society; reprinted with permission.\(^{33}\)
Figure 9: Scanning electron microscope image of MWNT array. Image courtesy of S.C. Parks.
4.1.2 Spin-Valves Prepared with Conventional Ferromagnets

Spin-valve devices are prepared at Ohio State from MWNT array material by directly depositing a layer of a conventional ferromagnet (Fe, Co, NiFe, and CoFe have been employed; Fe is described here) on the surface of the array. The MWNT array material contains some fissures and vacancies in macroscopic sized substrates, so a masking procedure is used to allow ferromagnet contact only in small, SEM inspected regions where the array is continuous and densely packed to avoid the possibility of a short circuit. A segment of MWNT array about 5 mm on a side is masked with 2-4
strands of 37 µm wide tungsten wire and ~500 nm SiO$_2$ is electron beam evaporated at a rate of .05-.1 nm/s. The sample is allowed to cool in the vacuum system and is then rotated 90° and re-masked with new tungsten wires. An additional 500 nm of SiO$_2$ are deposited under the same conditions and the mask wires are removed. In this way, active regions ~37 µm on a side remain exposed and the remainder of the MWNT array material is covered by at least 500 nm of insulating material, as verified by SEM [Figure 11]. The array is covered with a shadow mask, leaving ~1 mm$^2$ areas around each of the 4-16 active areas exposed and ~200 nm of Fe is deposited via electron beam evaporation at a rate of ~.1 nm/s. Individual top contacts (the 4-16 individual top FM layers) and a common bottom contact (the Cu film) provide electrical connection (schematic: [Figure 12], image of completed devices: [Figure 13]). The contacts are then connected to Cu wire by colloidal silver paste and the device is mounted in a configuration with the axes of the CNT along the direction of the applied magnetic field.
Figure 11: Scanning electron microscope image of MWNT array covered in SiO$_2$. The majority of the surface has a 1 µm layer of SiO$_2$; the visible vertical and horizontal stripes have received 500 nm of SiO$_2$; the central square (~40 µm x 40 µm) is uncoated for later deposition of Fe top contact.
Figure 12: Schematic representation of Fe/SiO$_2$-protected MWNT/iron nanoparticle spin-valve device.
Figure 13: Top view of a puck with sixteen SiO$_2$-protected MWNT array devices, allowing independent wiring of each (not pictured). Visible in the center of each Fe top contact (silver) are the outlines of SiO$_2$ patterning, revealing the location of each active device area.

4.1.3 Spin-Valves Prepared with LSMO

For devices incorporating LSMO, it is necessary to grow the two active portions of the device, the LSMO film and the CNT array, separately as their growth processes are incompatible. To grow the ferromagnetic film, an epitaxial 100 nm film of La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) on lattice matching pseudo-cubic (001) NdGaO$_3$ (NGO)
substrates is grown by pulsed laser deposition and capped with 3 unit cells (1.2 nm) of epitaxial LaAlO$_3$ (LAO) to improve interfacial quality between LSMO and MWNT. Interfaces between LSMO and metals$^{38}$ including carbon nanotubes$^{31, 39}$ often exhibit a tunnel barrier, indicated here by our device resistances of 10-100 kΩ for devices with many MWNT in contact. The roles of the thin LAO capping layer are (a) to provide superior protection of LSMO surface polarization than SrTiO$_3$ does,$^{40}$ (b) to promote efficient spin polarized carrier emission at the interface$^{23}$ and (c) to avoid LSMO surface contamination at the interface. After capping with thin LAO layer, samples are delivered from the University of Wisconsin to Ohio State University and kept inside an argon environment (O$_2$ < 0.3 ppm, H$_2$O < 1.0 ppm). The sample was treated by ultrasonic cleaning with a solvent chain consisting of acetone (3 min.), isopropyl alcohol (IPA) (3 min.), and DI water (3 min.) prior to further assembly.

Spin-valve devices are assembled by making a pressure contact between a piece of MWNT array material, grown as described in Section 4.1.1 and the cleaned LSMO film. Contact is made in a two-wire sense to the LSMO film and to the Cu film on the reverse side of the MWNT array [Figure 14]. These active portions of the device are then wrapped tightly in Kapton$^{	ext{®}}$ or Teflon$^{	ext{®}}$ tape and fixed in place with a small clamp made of a non-ferromagnetic material. Several such devices can be created in parallel on a single LSMO film sharing a single LSMO contact (but measured individually).
4.1.4 Spin-Valves Prepared from Aligned Arrays Grown in an Alumina Matrix

One variant of the ferromagnetic nanoparticle-driven spin-valve devices uses aligned CNT arrays grown in porous templates. Aluminum (purity 99.99%) is anodized in 0.2 M oxalic acid solution to form a porous anodic film ~10 μm thick with an average pore diameter of 40 nm, and an average pore spacing of 100 nm (center-to-center distance), as verified by scanning electron microscopy. Cobalt particles are then electrodeposited in the pores using a bath containing 50 g/l CoSO$_4$ and 25 g/l H$_3$BO$_3$. Following the Co deposition, carbon nanotubes are grown in the pores of the anodized aluminum oxide (AAO) by pyrolysis of acetylene at 630 °C. The electrodeposited Co particles serve as the first ferromagnetic layer in the spin-valve device. The ~10 μm thick AAO layer serves to protect the device from shorting after thermal deposition of the second ferromagnetic contact (which for the data shown is ~100 nm of Fe) followed by a capping layer of copper (~300 nm) [Figure 15]. This technique yields a regular array of
ferromagnetic nanoparticles and CNTs with well defined sizes and spacing [Figure 16], without any nanoscale manipulation, and allows for robust device construction.

Figure 15: Schematic representation of the device. Note the Co catalyst particles beneath the CNT array in the alumina pores serve as the second FM layer in the spin-valve structure. Pores have a diameter of 40 nm and a spacing of 100 nm. Copyright Elsevier, 2010. Reprinted with permission.
Figure 16: Scanning electron microscope image of cross-section of the as-grown CNT array in porous aluminum oxide template. Pores have a diameter of 40 nm and a spacing of 100 nm. Note the amorphous carbon on the surface of the anodized aluminum oxide. Copyright Elsevier, 2010. Reprinted with permission.

4.2 Measurement Methods and Equipment

Magnetotransport measurements were conducted using a Quantum Design Physical Properties Measurement System (PPMS) capable of producing magnetic fields in the sample chamber of its cryostat up to nine Tesla (±0.15 Oe under 9500 Oe, ±1.5 Oe over 9500 Oe). Temperature may be varied with the range of $1.7 \leq T \leq 350$ K. Designed for making resistivity and Hall measurements, the PPMS is computer controlled and for samples that can be measured within its power limitations, it can be programmed to run
long sequences. The PPMS is also adaptable for use with third party equipment. For device characterization, a sample is wired to a puck which has 12 electrical leads and provides thermal contact to the sample chamber. Wiring a sample to the puck, in this study, was accomplished by attaching thin copper wire to both the sample leads (one either to the Cu film backing or Al substrate, and one to either the LSMO or Fe film, as applicable) and then to the puck. Samples could be mounted either with films in-plane [Figure 17] or perpendicular to the plane [Figure 13] of the applied magnetic field, as specified for each particular experiment. The axis of the magnetic field is along the vertical axis of the puck.

Figure 17: Side view of a puck with vertically oriented device for magnetic field-in-plane measurement and typical wiring methods: indium contacts on the puck and colloidal Ag paste on the device.
Low voltage bias measurements take advantage of the PPMS automation (PPMS resistance uncertainty: \( \pm 1\% \) at 1 M\( \Omega \), \( \pm 5\% \) at 10 M\( \Omega \)). However, hardware limitations of \( V \leq 95 \) mV and a slow scan rate limited the utility of the built-in hardware in some cases, particularly for higher resistance or noise-prone samples, both of which benefit from higher applied voltages. For this, the open architecture of the PPMS was beneficial. A Keithley 2400 SourceMeter (\( \pm 0.09\% \) at 2 k\( \Omega \), \( \pm 0.13\% \) at 2 M\( \Omega \), \( \pm 0.66\% \) at 200 M\( \Omega \)) was operated through LabView programs to set the environment of the PPMS sample chamber and to acquire the transport data. For some devices with very low measured current, even at moderate applied voltages, care was needed in properly shielding the cabling to minimize noise and avoid transient noise sources. Some samples were measured remotely for this reason.

A superconducting quantum interference device (SQUID) magnetometer was used to compliment spin-valve magnetotransport measurements with magnetometry of the magnetic thin films and ferromagnetic nanoparticles. Saturation magnetization, exchange bias, and coercive field are routinely measured, the latter being especially important for spin valve characterization. These measurements were made in a Quantum Design Magnetic Properties Measurement System, capable of producing a nine Tesla (\( \pm 0.15 \) Oe under 9500 Oe, \( \pm 1.5 \) Oe over 9500 Oe) field with a temperature range of \( 2.0 \leq T \leq 350 \) K.
Chapter 5: Study 1: Spin-Valves Incorporating Aligned Arrays of Carbon Nanotubes, Metallic Nanoparticles, and Conventional Ferromagnetic Films

Several different techniques can be used to create a spin-valve that incorporates an aligned array of carbon nanotubes as a NM spin transport layer. Here are described the results from two methods using a directly deposited film of a traditional ferromagnet, iron, and the catalyst FM nanoparticles used to grow the nanotubes. Early efforts, described elsewhere,\(^{14}\) relied on pressure contacts that were difficult to maintain through cooling/heating, mechanical upsets, and harder to reproduce (perhaps 1% device yield). This lead to a search for more reliable designs and ones that would be less prone to infiltration by unwanted ambient agents (e.g. \(O_2\)). First, we consider freestanding arrays that have been masked with SiO\(_2\) to leave only a small contact area exposed. Next we consider arrays that have been grown in the pores of an alumina matrix, giving the nanotubes a uniform spacing, diameter, and length and protecting the catalyst FM (Co) particles and CNT.

5.1 Spin-Valves from Freestanding Aligned Arrays

Spin-valve devices are prepared, incorporating aligned array of MWNT with Fe growth catalysts and a top-deposited Fe layer as described in Section 4.1.2. Arrays prepared in this fashion have a thick layer of SiO\(_2\) preventing undesired contact between
the Fe top layer and lower portions of the MWNT, the Fe nanoparticles, or the Cu substrate. After very low functional device yields in pressure-contact devices and various unmasked or soft-material masked (e.g. photoresist, polystyrene) configurations, this SiO$_2$-coating procedure quickly produced robust results and we were able to measure magnetoresistance with hysteretic switching (i.e. spin-valve behavior) in devices fashioned from several separately grown MWNT arrays.

Initial devices produced using this technique exhibited negative magnetoresistance approaching 15% at 2 K [Figure 18]. A sharp decrease in resistance is seen at ~275 Oe applied field when the thin Fe film switches magnetization direction. This reduced resistance is maintained until ~450 Oe where Fe nanoparticles begin to switch the direction of their magnetization. This is a more gradual process and continues until ~800 Oe at which point all the Fe nanoparticles have realigned. The Fe nanoparticles have a range of sizes, dictated by the diameter of the nanotube that they inhabit, affecting their coercive fields. For this reason, the nanoparticles do not switch magnetization direction as an ensemble. This switching of magnetization is hysteretic and symmetric and presents the “double peak” shape that is indicative of spin-valve behavior. Nanotubes in this array had a length of 10 $\mu$m, as shown in Figure 9.
Figure 18: Magnetoresistance, defined as \( (R_{ap} - R_p)/R_p \) (right axis) and resistance (left axis) versus field for low-resistance Fe nanoparticle/SiO\(_2\)-protected MWNT array/Fe device at 2 K and 100 \( \mu \)V applied bias, showing up to -15\% change in resistance.

The maximum expected magnetoresistance for a given set of FM electrodes (that is, with no loss of spin polarization between them) can be calculated using Julliére’s model\(^{12}\) as in Equation 11. Here, \( P_1 \) and \( P_2 \), the spin polarizations of the electrodes, are both Fe (\( P \sim 44\% \)). For two iron electrodes, the maximum expected magnetoresistance is 32.4\%. Using our observed magnetoresistance of 15\%, the calculated maximum possible MR of 32.4\% and the measured array length \( \ell = 10 \) \( \mu \)m, we calculate the minimum spin diffusion length through the CNT, \( \ell_s \), to be 13 \( \mu \)m. Again, this represents a minimum as any interfacial effects will decrease the effective spin polarization of the current entering or exiting the CNT. This magnetoresistance decreases with increased temperature, disappearing by 5 K for the device in Figure 18. Likewise, the observed
MR decreases as bias across the device is increased from $V_b = 100 \, \mu V$ and all but disappears with $V_b = 7.9 \, mV$ [Figure 19]. Decreases in observed MR with increased bias and temperature have been widely observed in single-CNT devices in similar temperature and potential ranges.

Figure 19: Applied bias ($V_b$) vs. magnetoresistance (MR) in Fe nanoparticle/SiO$_2$ protected MWNT array/Fe device.

Several devices fabricated and measured in this fashion have very low resistances, as described in the preceding passage. Such a low resistance indicates that many CNT are involved in the transport of current through the device, even in the improbable case of
exquisitely contacted MWNT as described in Section 2.2.4. A more likely scenario is that few shells (or only one shell) of the MWNT are involved in charge and spin transport, that contact resistances (to include tunnel barriers, Coulomb blockade, etc.) are large, that transport through 10 µm-long CNT is not fully ballistic, and therefore that a large multiplicity of nanotubes are involved. Large device resistances in single-MWNT devices back up this second scenario. Other devices fabricated in this fashion had much higher resistances, but still demonstrated similar magnetoresistive effects [Figure 20] and had similar temperature and bias dependences.

Figure 20: Magnetoresistance (right axis) and resistance (left axis) versus field for high-resistance Fe nanoparticle/SiO$_2$ protected MWNT array/Fe device at 2 K and 10 V applied bias, showing up to -3% change in resistance.
5.2 Spin-Valves from Aligned Arrays Grown in an Alumina Matrix

A major difficulty in creating a spin-valve (or any similar device) from an aligned array of nanotubes is the propensity of any layers directly deposited on the array surface to penetrate well into the bulk of the array, especially where cracks, fissures, or voids appear in the array. As described above, one method that can be used is to limit the contact area and choose spaces that are defect free. This addresses the second, device-fatal, condition, but does not totally prevent the penetration of electrode material past the very ends of the array. Taking this masking idea further, it is possible to prepare arrays that have been grown totally within the volume of a resistive material. Under the right electrochemical etch conditions (see Chapter 4), high-purity aluminum develops evenly-spaced nanoscale pores and oxidizes to leave an alumina matrix [Figure 16]. A MWNT array grown in such an array will grow to match the pore diameter and thus be of a higher uniformity of spacing, size, and length (terminating at the AlO\textsubscript{x} surface) and will be protected from infiltration by top-deposited materials. There are several drawbacks, however. The aluminum growth medium limits the temperature range for CVD growth of CNT- the growth conditions used for devices in Section 5.1 and in Chapter 6 would melt aluminum. This leads to higher amounts of amorphous carbon deposited on the surface of the array, and to a higher defect rate in CNT growth.\textsuperscript{34,44} Second, an unavoidable layer of AlO\textsubscript{x} is created at the bottom of the pores during etching. This guarantees a tunnel barrier at this end of the device and gives a higher minimum resistance for any device fabricated in this manner.
Each Co nanoparticle/CNT array/Fe device is examined in a similar way to the devices in Section 5.1, with a MR ratio defined as above. The device is cooled in zero applied magnetic field from 300 K to 15 K for measurements. Resistance is measured in a two-terminal configuration at an applied bias current \( i_B \) of 10 nA. The applied magnetic field is first swept from +5000 Oe to −5000 Oe and then back to +5000 Oe with resistance measured at regular intervals. The measured device resistance during cooling for devices using the AAO template is within the range of resistance data we found for freestanding arrays above as well as LSMO/array devices described in Chapter 6 reported and similar to resistances measured for CNT arrays formed in this manner using non-magnetic electrodes.\(^{45}\) The current-voltage characteristics for this device are observed to be nonlinear for all temperatures measured, up to 50 K. As expected with the known AlO\(_x\) layer, the nonlinear current-voltage characteristic and the high device resistance for a device containing many parallel MWNT indicate tunnel junction behavior.\(^{31}\) The Co nanoparticles at the bottom of the pores and the Fe deposited on top have similar coercive fields at the temperatures measured. This is the likely cause of a less clear switching effect [Figure 21 (a)] than the results from the above SiO\(_2\)-protected Fe film/CNT/Fe nanoparticle devices and for earlier CoFe/CNT/Fe nanoparticle pressure contact devices.\(^{14}\) The temperature stability of the AAO device is much higher than that for (Fe or CoFe)/freestanding array/Fe nanoparticle devices,\(^{14}\) such as those above, and exhibit a spin-valve effect for temperatures up to 50 K [Figure 21 (b)], whereas the devices in Section 5.1 had no observed magnetoresistive effects above \( \sim 10 \) K. The reduced magnitude of the effect in the AAO template devices is attributed to several factors.
First, the small difference in coercive fields could make a fully antiparallel state unlikely. In addition, the CNT arrays formed by this low temperature method often contain more structural defects and amorphous carbon coated on the top of the CNT array (as visible in Figure 16), leading to an increased number of scattering centers within the array and at the interface.\textsuperscript{34} This probable interfacial resistance from the presence of amorphous carbon may lead to the observed nonlinearity of the device’s current-voltage characteristics as mentioned above.\textsuperscript{44} While the magnitude of the magnetoresistance is smaller than for the freestanding array devices, the effect persists for temperatures up to 50 K. Compared to spintronic devices formed from individual nanotubes,\textsuperscript{13, 14, 46} the device formed using the AAO CNT array exhibits weak temperature dependence over the entire measured temperature range, suggesting that improvements in device design could lead to device operation at much higher temperatures.

![Figure 21](image-url)

Figure 21: (a) Magnetoresistance (right axis) and resistance (left axis) versus field for Co nanoparticle/AlO\textsubscript{x}-embedded MWNT array/Fe device at 40 K and 10 nA bias current (b) Temperature dependence of magnetoresistance for device in (a) up to 50 K. Copyright Elsevier, 2010. Reprinted with permission.
Spin scattering length can be calculated as in Equation 11 with polarizations for Fe ($P_1 \sim 44\%$) and Co ($P_2 \sim 63\%$). Magnetoresistance reaches a maximum of $\sim 1.5\%$ for the device in Figure 21 (a). Using focused ion beam (FIB) cross-sectioning and scanning electron microscope (SEM) images, the length of the CNT array is determined to be $\ell = 10 \, \mu m$, giving an estimated minimum of $\ell_s = 2 \, \mu m$ at 40 K. This value is smaller than that found above for the SiO$_2$ prepared freestanding arrays. Again, given the presence of uncertain injection efficiencies due to impurities at the CNT/FM interface, this spin diffusion length should be considered a lower bound on the actual spin diffusion length of the CNT array itself. Although the effects of the interface and actual spin scattering mechanisms within the CNT are not distinguishable via this MR measurement, it is reasonable to expect that nanotubes grown in an AlO$_x$ matrix would have shorter spin diffusion lengths due to a lower growth temperature as noted above, leading to more defects which would serve as spin scattering sites.
In spin-valves fabricated from traditional ferromagnets, we must be concerned with the relatively low polarization of the FM electrodes as a source of spin-polarized current. Nearly fully spin polarized materials such as LSMO (see Section 3.2) have been shown to be effective at highly polarized spin injection for a diverse set of spin transport media including small-molecule organics\textsuperscript{24} and MWNT.\textsuperscript{31, 39} Because LSMO (epitaxially grown by pulsed laser deposition) and CNT (grown from iron catalysts by chemical vapor deposition) have incompatible growth environments (CNT will not form on LSMO and the LSMO will not survive the required temperatures) and conformations (LSMO requires a lattice-matched, ultraclean substrate, which a CNT array is most certainly not), the two layers much be grown separately and combined mechanically. The pressure contact used to bind them is, as previously mentioned, not ideal for reasons of mechanical stability, particularly under temperature changes. However, as the components of this particular system are air-stable, some of the difficulties with traditional ferromagnetic film pressure contacts are avoided.

Spin-valve behavior has previously been demonstrated in devices utilizing individual MWNT between two LSMO electrodes,\textsuperscript{31} exhibiting a large positive MR. To make use of this new highly spin polarized material, we constructed devices as described in
Section 4.1.3 and depicted in Figure 14 from the same array material as used for SiO$_2$-coated Fe film spin-valves in Section 5.1. Measurements of the magnetization of the MWNT array [Figure 22] show that the nanoparticles have a coercive field $H_c = 750$ Oe at 2 K, decreasing to ~125 Oe at room temperature. Saturation is not reached until several thousand Oersted [Figure 23 (left)], indicating that the aggregate of Fe nanoparticles do not switch magnetization direction at a uniform field. This is expected from the variety of nanoparticle sizes (corresponding to CNT diameters in Figure 10), and the strong dependence of $H_c$ on nanoparticle size\textsuperscript{19} and the orientation of the long axis relative to the applied magnetic field. This indicates that the Fe nanoparticles (considered as a single layer) do not form a single large domain or even a few domains per device, but rather small cluster domains or single-nanoparticle domains. Similar measurements [Figure 22] of the LSMO film show $H_c = 230$ Oe at 10 K, decreasing to ~25 Oe at room temperature, allowing clear distinction between the switching of the LSMO and the switching of the Fe nanoparticles at room temperature down to 10 K. Below this temperature, the paramagnetic NGO substrate begins to dominate the magnetization of the NGO/LSMO/LAO multilayer, complicating the assignment of a clear coercive field for the multilayer as a whole [Figure 23 (right)].

The device is cooled in zero applied magnetic field to 2 K. Resistance is measured at applied voltages ($V_b$) of 10 mV-5 V and at temperatures from 2 K progressively up to 100 K. Magnetic field is swept from -1000 Oe to 1000 Oe and back with resistance measured at regular intervals. In some cases magnetic field sweeps are extended up to ±2 T to verify that no MR effects appear past ±1000 Oe. We observe a
decrease in resistance as large as 31.5% [Figure 24] at 50 K and 1 V bias. This MR is comparable to that measured in individual\textsuperscript{13, 19, 47, 48} and array\textsuperscript{14} MWNT devices with Fe (Section 5.1) or Co-based ferromagnetic electrodes and is, as expected, somewhat smaller than the maximum magnitude reported for all-LSMO\textsuperscript{31} individual MWNT devices due to the lower polarization of the Fe-nanoparticle-based electrode\textsuperscript{43} relative to a second LSMO electrode. It should be noted that this similar MR value was achieved over a much longer transport path ($\ell \sim 10 \mu$m), indicating again that the limit to the spin-polarized transport is dependent upon injection at the FM/MWNT interface rather than MR effects intrinsic to the MWNT.

![Ferromagnetic Component Coercive Field](image)

Figure 22: Coercive field for iron nanoparticles and 100 nm LSMO film grown on NGO.
Figure 23: Hysteretic behavior of Fe nanoparticles (left) and LSMO (right). Notice the complicated magnetization behavior for LSMO and its NGO substrate below 10 K.
Figure 24: Magnetoresistance (right axis) and resistance (left axis) versus field for LSMO/MWNT/Fe nanoparticle device at 50 K and 1 V applied bias, showing up to -31.5% change in resistance, typical of observed negative-only MR behavior for LSMO devices.

Employing Equation 11 with an assumption of $P_{LSMO} = 95\%$, -31.5% MR indicates a minimum $\ell_s \approx 15.6 \, \mu m$ and an assumption of $P_{LSMO} = 80\%^{22}$ indicates a minimum $\ell_s \approx 19.3 \, \mu m$. As before, any contact or other resistance within the device external to the FM/NM/FM layers would indicate an even higher local MR and a correspondingly longer $\ell_s$, as has long been noted.$^{17}$

In contrast to the main results produced in Chapter 5 and heretofore in this chapter, we observe in some cases the occurrence of large, positive MR as the spin-valve device approaches zero magnetic field, rather than the more common resistance transitions occurring after a device has been subjected to a switch in field direction. This
effect occurs in addition to the above described negative MR, yielding a device that exhibits regions of positive and negative MR in a single sweep of magnetic field [Figure 25] at low temperatures. For the device in Figure 25, $\Delta R/R_p$ reaches a maximum of $\sim$10%, measured at 5 K. Similar combined pre- and post-zero MR effects have been described by others\textsuperscript{49} and exhibited to some extent in many studies, particularly those that are gate-tunable, a parameter that the array geometry does not allow. To our knowledge no fully satisfactory model has been given. We propose a plausible mechanism that could produce this effect. At low temperatures the magnetization of the LSMO on NGO is complex and decreases sharply well before reaching zero field and increases again before finally switching directions completely at high field (see Figure 23 (right)). This would affect the spin polarization of the electrode and thus the MR exhibited by the device.
Figure 25: Magnetoresistance (right axis) and resistance (left axis) versus field for LSMO/MWNT/Fe nanoparticle device at 5 K and 1 V applied bias, showing up to -10% and +10% changes in resistance in different field regimes. This is explained by the complicated nature of the magnetization of the NGO/LSMO substrate at low temperatures (cf. Figure 23 (right)).

The magnetoresistance is found to remain near maximum levels from $V_{\text{bias}} = 10$ mV up to several volts, but falls off sharply above 4 V. We find that the large negative MR persists up to 50 K, where the positive MR persists from 2 K up to 20 K and disappears by 50 K, with both species of MR becoming undetectable by 100 K, after which noise effects overwhelm any remaining < 5% effects. The behavior above 50 K is consistent with other LSMO-based spin-valve devices and the observed suppression of the surface spin polarization in LSMO films.\textsuperscript{30,50}
In conclusion, we have observed spin-dependant transport in spin-valves constructed from nearly-fully-spin-polarized films of LSMO and aligned arrays of MWNT up to 10 $\mu$m in length, with observed resistance changes in excess of 30%, indicating efficient spin injection from the LSMO and effective long-distance spin-coherent transport through the MWNT array. Spin diffusion lengths in this array are calculated to be at least 15.6 $\mu$m.
Chapter 7: Conclusions and Further Work

7.1 Summary and Conclusions

Carbon nanotubes had previously been demonstrated to been an excellent spin-transport material. Early work involved single nanotubes and required precise lithography. Here we have demonstrated spin-valve devices fabricated from aligned arrays of carbon nanotubes, allowing relatively simple top-down fabrication and demonstrating excellent spin transport, with very long spin diffusion lengths reaching at least 15 µm. We further innovate upon early designs by making use of the ferromagnetic nanoparticles that are the growth catalysts from which the carbon nanotubes form, obviating the addition of a second deposited ferromagnetic layer. Difficulties in protecting array material from short-circuiting are remedied by way of after-growth addition of an insulating SiO$_2$ layer, growth of the array in a porous, insulting AlO$_x$ matrix, or utilization of an air-insensitive highly spin polarized material such as LSMO. This last method is of additional interest as a means of achieving very highly spin-polarized injection into the CNT array, leading to observed magnetoresistances in excess of -30%, persisting to at least 50 K. In all presented cases, magnetoresistance changes correspond well with the coercive field of the chosen ferromagnetic materials. The novel use of carbon nanotube arrays and their ferromagnetic catalyst nanoparticles represent a significant advance in the available materials with which to study spin phenomena and
the combination of this geometry with half-metallic LSMO films has lead to nearly macroscopic spin diffusion lengths.

7.2 Further Research

There are several directions that continued research could build upon these results. The most direct continuation is further variation of the ferromagnetic or spin-polarized materials in the spin-valve. For instance, the highly spin polarized organic ferromagnet vanadium tetracyanoethylene V[TCNE]x-2, and its family of materials present possible spin injecting materials to replace the Fe film, with their ability to conform to the surface of the array, and LSMO for its high spin polarization. Further process refinement of the SiO2-masking process could allow for the design of more complicated logic structures utilizing multiple parallel devices, perhaps with different top ferromagnets (and thus different switching fields). Although single-walled nanotubes have generally been harder to incorporate in spin dependent devices, the simplicity of SWNT as a spin and charge transport path are another obvious area of study. Individual-SWNT spin-valves have been demonstrated elsewhere and implementation of array-based devices would utilize the techniques above and the model system presented by SWNT. Alumina-grown array devices, with their high uniformity of CNT spacing and length, could also lead to multi-element structures or many separate elements run in a highly parallel configuration. Inclusion of light-emitting elements at the top of array spin-valves could potentially be used as a source of spin polarized light, and high bias arrays could be an emission source of spin polarized electrons.
References