Magnetic Domain Configurations and Huge Wall Resistivity in Half-metallic Chromium Dioxide (CrO$_2$) Nanostructures

by

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To my dearest parents,

whom I love, honor and thank

from the bottom of my heart
**Abstract** of "Magnetic Domain Configurations and Huge Wall Resistivity in Half-metallic Chromium Dioxide (CrO₂) Nanostructures", by Xiaojing Zou, Ph. D., Oct. 2009

We have fabricated, studied and compared the electrical and magnetic behavior of several sub-micron-sized polycrystalline and epitaxial chromium dioxide (CrO₂) nanostructures, grown using selective-area growth technique.

Magnetic domain structures were studied by magnetic force microscopy, and in-plane, lamellar domain structure with fragmented walls aligned along the magnetic easy axis direction have been observed, indicating the existence of a large magnetocrystalline anisotropy in epitaxial CrO₂ nanostructures. Low-temperature transport measurements on nanowires have shown that the dc resistivity of polycrystalline CrO₂ wires is strongly dependent on the linewidth. Below a critical temperature, a transition from a positive to a negative temperature coefficient of resistivity have been observed, which we attribute to a competition between the scattering of the conduction electrons inside the grains and scattering across the grain boundaries. Using a model based on grain boundary scattering, we estimate a mean transmission probability through the grain boundaries to be on the order of $10^{-1}$. Furthermore, magnetoresistance (MR) measurement indicates that the MR behavior of polycrystalline CrO₂ wires is dominated by the shape anisotropy; however, for epitaxial CrO₂ wires, both the shape and magnetocrystalline anisotropy play important roles, and the resulting MR properties are found to be closely related to the orientation of the wire axis. By studying the MR curves, we inferred the internal magnetic domain structures in various single crystal CrO₂ wires and found that the spin-dependent transport is much stronger across a grain boundary than a magnetic domain wall.
We have also studied the magnetotransport properties of CrO$_2$ nanoscale continuous contacts. Manipulating the domain walls using a large dc current in the contact area yields a magnetoresistance of up to 25%, which is the largest ever seen in a single ferromagnetic film. The single domain-wall-resistance (DWR) is determined to be three orders of magnitude larger than that of conventional 3$d$ ferromagnets, as a result of the material's half-metallicity. We have measured DWR and the spin-torque effect along different crystallographic axes and at varying temperatures. Finally, we present the results of a theoretical analysis of this system, based on its half-metallic character and on the intrinsic magnetic behavior of CrO$_2$. 
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Chapter 1

Motivation and Outline

1.1 Motivation

Driven by the tremendous improvements in the technology available for the deposition and characterization of ultrathin films and multilayers of various materials, as well as the capabilities to pattern these films into nanoscale devices, rapid progress has been made in the area of nanostructured materials during the past two decades, which provide the critical building blocks for the booming nanoscience and nanotechnology. These materials typically have structural or chemical restrictions on nanometer scale along one or more of the dimensions. Due to their extremely small length scale and low dimensionality, they often exhibit novel and enhanced properties over their bulk counterparts [1].

Recent progresses on magnetism and magnetic materials have made magnetic nanostructures a particularly interesting class of materials for both scientific and technological explorations. For example, studies on subjects such as giant magnetoresistance
(GMR) [2,3], magnetic tunneling junctions (MTJs) [4,5], half-metallic ferromagnets [6], spin-injection [7] and current-induced magnetization switching [8] have led to an exciting subject called spintronics, where the electron spin (together with the charge) plays an active role in storing and transferring information [9].

In the area of spintronics, ferromagnets with high spin polarization are of significant importance [9,10]. However, the measured spin polarization of traditional ferromagnets (e.g., Fe, Co, and Ni) is only around 40% – 50% [11]. Using theoretical calculations, physicists have predicted the existence of so-called half-metallic ferromagnets (HMFs), which have an energy gap at the Fermi level $E_F$ in one of the two spin channels and thus can exhibit 100% spin polarization. The experimental realization of truly half-metallic materials has the potential to allow major advances in spintronics, since the performance of most devices improves dramatically as the spin polarization of the metal approaches one. For example, highly spin polarized ferromagnets enable the injection of electron spins from a ferromagnetic metal into a semiconductor with high efficiency [7], as well as an enormous increase in the tunneling magnetoresistance ratios of MTJs [12].

This exciting half-metallicity has been predicted for a number of materials, such as certain Heusler alloys, manganese perovskite La$_{0.7}$Sr$_{0.3}$MnO$_3$ [13], magnetite Fe$_3$O$_4$ [14], and chromium dioxide CrO$_2$ [15]. However, till now, the half-metallicity of most of these materials has yet to be demonstrated, with CrO$_2$ as the only material which has been unambiguously determined to be half-metallic [11,16].

Although numerous studies on the properties of chromium dioxide have been conducted in the past several years [17,18,19], most of this research has been focused on continuous bulk films. Nevertheless, the magnetic behavior of ferromagnetic systems is
closely related to a material’s size and dimensionality. When the physical size of a magnetic system is reduced to dimensions comparable to, or even smaller than, certain characteristic lengths (domain wall width, exchange length, spin diffusion length, etc.), unexpected and/or novel behavior is often observed [1]. For examples, the magnetization reversal processes can be drastically modified in magnetic structures confined to sizes that preclude the domain wall formation [20]. Among the many different varieties of magnetic nanostructures, nanodots and nanowires are attracting a great deal of attention due to their distinctive properties and potential application as ultrahigh density magnetic recording media [21,22].

Furthermore, with the constant demand for miniaturization in the field of spintronics, conventional way of switching magnetic configuration by magnetic field have shown several drawbacks. Typically the switching field increases with decreasing device dimension [20], which in turn boosts the risk of cross talk and energy consumption. In recent years, a novel magnetization switching mechanism has been discovered, where the orientation of magnetic moments can be altered (e.g., magnetization reversal in GMR and MTJ, displacement of single domain wall) by applying a large spin polarized current due to the spin momentum transfer [23,8]. This effect, also known as spin-torque effect, shows potential for novel memory devices based on domain wall physics as it could simplify designs by eliminating magnetic field-generating circuits. Additionally, it has been discovered that a nanocontact structure could pin domain wall(s) as defect(s) due to spontaneous magnetization, and a few experiments have been carried out to study the spin dependent electron transport properties of ferromagnetic nanocontacts [24,25]. However, most of these researches adopted the geometry confinement (shape anisotropy) as the only
way to control the domain wall configuration, and the observed current-induced resistance changes are very small in nanocontacts made by traditional ferromagnets.

Unlike conventional magnetic materials, chromium dioxide has the advantage of being made into epitaxial form easily by chemical vapor deposition [26]. By controlling the geometrical size and crystallographic orientations of single crystal CrO\textsubscript{2} nanostructures, diverse domain structures are expected, due to the competition between the shape and magnetocrystalline anisotropy terms. This makes it possible to investigate the physics related to the domain wall and its mobility in a more efficient way. Therefore, the behavior of half-metallic chromium dioxide nanostructures is of significance both in terms of understanding the fundamental physics of half-metals, and for the development of new spintronic applications.

1.2 Outline

In this thesis, we present a novel method to fabricate submicrometric chromium dioxide (CrO\textsubscript{2}) nanostructures, both in polycrystalline and epitaxial forms. The use of so called selective-area growth technique for patterning small elements avoids the degradation of the CrO\textsubscript{2} film caused by the commonly applied etching process. We systematically studied the electrical, magnetic and magnetotransport properties CrO\textsubscript{2} nanodot and nanowire structures. Our results show that other than the shape anisotropy, the magnetocrystalline anisotropy also plays an important role in CrO\textsubscript{2} nanostructures. Furthermore, we have also studied the physical properties of half-metallic epitaxial CrO\textsubscript{2} nanocontact structures and found a magnetoresistance of up to 25%, which is the largest ever seen in a
single ferromagnetic film. The single domain wall resistance (DWR) is determined to be three orders of magnitude larger than that of conventional 3d ferromagnets, as a result of the material's half-metallicity.

The thesis is organized as follows:

**Chapter Two** gives a general background on the basics of magnetism with emphasis on the concept of spin polarization and half-metallicity from the density of states (DOS) point of view. We also discuss major types of magnetoresistance including anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR) and tunneling magnetoresistance (TMR), focusing on the possible enhanced MR effect by introducing half-metals into these structures. Several candidates that have been theoretically predicted to be half-metallic are reviewed with their most recent experimental results. Finally, the bulk properties of chromium dioxide (CrO$_2$) are briefly described as the background for the author’s Ph. D. work.

**Chapter Three** introduces the origin of magnetic domains and domain walls, as a consequence of the competition between different magnetic energy terms. Theoretical results regarding the properties of domain wall thickness and resistivity (DWR) are briefly reviewed with emphasis on the Levy and Zhang’s model. On the other hand, some of the novel properties, emerging when the size of ferromagnets are reduced down to nanometer scale, are described. Finally, a relatively new phenomenon, called spin torque effect, is discussed, serving as the theoretical basis for the last Chapter.

**Chapter Four** describes the fabrication techniques used in this work, including deposition methods (MOCVD, EBE, sputtering), lithography (optical and e-beam), etching (wet etching, RIE and IBE). It will also discuss some characterization methods such as
X-ray diffraction, SEM, MFM and VSM. Finally, the low temperature electric transport measurement system in our lab will be described.

**Chapter Five** provides the detailed fabrication processes of both polycrystalline and single crystal chromium dioxide nanostructures, focusing on the advantages of using selective-area growth technique. Furthermore, the morphological comparison between these nanostructures and the anisotropic lateral growth rate of epitaxial chromium dioxide nanocrystals is investigated.

**Chapter Six** studies the magnetic domain structures of submicrometric epitaxial CrO$_2$ elements by magnetic force microscopy. The observed in-plane, lamellar domain structure with fragmented walls aligned along the magnetic easy axis direction is analyzed using a classical model for ferromagnetic materials with a uniaxial anisotropy. Estimates of the domain wall energy density and exchange stiffness constant for CrO$_2$ are obtained.

**Chapter Seven** studies and compares the electrical and magnetic behavior of sub-micron-sized polycrystalline and epitaxial chromium dioxide wires. Low temperature transport measurement results are analyzed using a semi-classical model based on grain boundary scattering, and an estimation of the mean transmission probability through grain boundaries is obtained. Low field magnetoresistance values are also presented with emphasis on the corresponding domain structures, which result from the competition between shape and magnetocrystalline anisotropy.

**Chapter Eight** studies the magnetotransport properties of half-metallic epitaxial chromium dioxide nanoscale continuous contacts. We find a magnetoresistance as high as 25% by manipulating the domain walls using a large dc current in the contact area yields, which is the largest value ever seen in a single ferromagnetic film. The single domain wall
resistance (DWR) is determined to be three orders of magnitude larger than that of conventional 3d ferromagnets, as a result of the material's half-metallicity. The measured DWR and the spin-torque effect along different crystallographic axes and at varying temperatures are discussed. Finally, we present the results of a theoretical analysis of this system, based on its half-metallic character and on the intrinsic magnetic behavior of CrO$_2$. 
Chapter 2

Spin Polarization and Half Metallic Chromium Dioxide (CrO₂)

In the last two decades, stimulated by the discovery of large magnetoresistance at room temperature, a large effort has been put into the development of new classes of magnetically engineered thin-film materials, and as a consequence, a new subject called spintronics emerges, where the electron spin plays an active role in storing and transferring information [10]. Some concepts such as giant magnetoresistance (GMR), magnetic tunneling junctions (MTJs), spin polarization (SP) and half-metallicity (HM), lie in the heart of spintronics, and are discussed in this Chapter with most of the emphasis placed on a specific material – chromium dioxide (CrO₂) which is currently the only experimentally confirmed half-metal and also the main research subject of the author’s Ph. D work.
2.1 Magnetism and Spin Polarization

2.1.1 Paramagnetism

In normal metals without an external magnetic field, there is no privileged spin orientation, i.e. spin-up and spin-down electrons are symmetric, such as copper whose density of states (DOS) is shown in Figure 2.1. One can achieve the spin band splitting using an external magnetic field $H$. If we assume that all the atoms are in the ground state with the angular momentum $J$ (quantum number), using Boltzmann Statistics the magnetization $M$ of this material can be written as:

$$
M = N \sum_{M_J = -J}^{J} \frac{-M_J g \mu_B e^{M_J g \mu_B H / k_B T}}{\sum_{M_J = -J}^{J} e^{M_J g \mu_B H / k_B T}} = N g \mu_B J B_J(x) \quad x = \frac{g \mu_B H}{k_B T} \quad \ldots . . . . (2.1)
$$

$$
B_J(x) = \left[ (2J + 1)/2J \right] \coth \left[ (2J + 1)/2J \right] x - (1/2J) \coth(x/2J)
$$

where $N$ denotes the number of atoms, $g$ is the gyromagnetic factor, $\mu_B$ is the Bohr magnetron and $M_J$ is the quantum number of the angular momentum.

In the high field limit ($H \to \infty$), $B_J(x) \to 1$ and thus $M \to N g \mu_B J$, which means the saturation state for this material. While in the high temperature limit where $x \to 0$, we have $B_J(x) \to (J+1)x/3J$ and $M \to N g^2 \mu_B^2 J(J+1)H/3k_B T$. For most nonmagnetic materials at room temperature, the high temperature limit approximation is valid. Therefore, the shape of Figure 2.1 will not be substantially changed by external field (in Tesla range) in normal conditions. Also, the Curie’s Law is obvious here, i.e. the susceptibility $\chi = M/H \sim 1/T$. 
2.1.2 Ferromagnetism

When neighboring electrons interact with each other through their spin degree of freedom (exchange interaction), spontaneous magnetic ordering can occur. Two physical effects, i.e. Pauli exclusion principle and Coulomb repulsion, are responsible for the origin of this interaction. As it turns out, for many systems the exchange Hamiltonian can be written as (Heisenberg Hamiltonian):

$$H_{\text{spin}} = - \sum J_{ij} \hat{S}_i \cdot \hat{S}_j$$

(2.2)

where $J_{ij}$ represents the strength of the direct exchange interaction. This Heisenberg exchange energy term can lead to preferred spin parallel or anti-parallel alignment between neighboring atoms, resulting in an effective molecular field in the material, i.e. spontaneous magnetization. Depending on the positive or negative sign of the exchange energy constant $J_{ij}$, this spontaneous ordering can be classified as *ferromagnetism* (FM), in which

![Figure 2.1. Calculated density of states in copper (taken from Ref. [27]).](image)
spins prefer to align parallelly, *antiferromagnetism* (AFM), in which spins prefer to align antiparallelly, as well as *ferrimagnetism*, in which antiparallel alignment of spins with different magnitude produces a net magnetization. Summary of all these types of magnetism are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Types of Magnetism</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>$S = 0$, only orbital magnetic moment</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>$S \neq 0$, no interatomic interaction</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>$S \neq 0$, interatomic parallel coupling ($J &gt; 0$)</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>$S \neq 0$, interatomic antiparallel coupling ($J &lt; 0$)</td>
</tr>
<tr>
<td>Ferrimagnetism</td>
<td>$S \neq 0$, interatomic antiparallel coupling with different atomic moments</td>
</tr>
</tbody>
</table>

Table 2.1. Table of the features for different types of magnetism.

In these ferromagnetic materials, the symmetry is broken and this asymmetry splits the density of states into two distinctly different distributions. As evidenced in the case of iron (Fe), shown in Figure 2.2, this asymmetry changes the density of states at the Fermi level for spin-up and spin-down electrons, resulting in a net spin population in a preferred direction.
2.1.3 Spin Polarization

There is a parameter defined as a representation of the spin asymmetry in a ferromagnet, i.e. spin polarization $P$, which is in general given by:

$$ P = \frac{n_{\uparrow} - n_{\downarrow}}{n_{\uparrow} + n_{\downarrow}} \tag{2.3} $$

where $n_{\uparrow(\downarrow)}$ is the corresponding density of states of spin-up (spin-down) electrons at the Fermi level. This quantity measures the excess of carriers of the majority spin over the minority spin as fraction of the total number of carriers. The value of $P$ varies between -1 and +1, with $P = 0$ for a non-magnetic metal and $P = 1$ for a perfectly polarized material (half-metal). For 3$d$ transition metal ferromagnets, the typical spin polarization values are
between 0.3 - 0.5. Table 2.2 lists some recently measured spin polarization values for common ferromagnetic materials.

<table>
<thead>
<tr>
<th>FM material</th>
<th>Spin polarization (P)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>45%</td>
<td>[28]</td>
</tr>
<tr>
<td>Co</td>
<td>42%</td>
<td>[28]</td>
</tr>
<tr>
<td>Ni</td>
<td>33%</td>
<td>[28]</td>
</tr>
<tr>
<td>Ni_{80}Fe_{20}</td>
<td>32 - 48%</td>
<td>[29,28]</td>
</tr>
<tr>
<td>Ni_{40}Fe_{60}</td>
<td>55%</td>
<td>[30]</td>
</tr>
<tr>
<td>Co_{50}Fe_{50}</td>
<td>55%</td>
<td>[30]</td>
</tr>
<tr>
<td>Co_{84}Fe_{16}</td>
<td>55%</td>
<td>[28]</td>
</tr>
<tr>
<td>La_{0.7}Sr_{0.3}MnO_{3}</td>
<td>54%</td>
<td>[31]</td>
</tr>
<tr>
<td>Co_{2}MnSi</td>
<td>56%</td>
<td>[32]</td>
</tr>
<tr>
<td>Fe_{3}O_{4}</td>
<td>40%</td>
<td>[33]</td>
</tr>
<tr>
<td>CrO_{2}</td>
<td>98%</td>
<td>[11,6,34]</td>
</tr>
</tbody>
</table>

**Table 2.2.** Table of the spin polarization values of common ferromagnetic materials.

The asymmetry in the densities of states leads to spin-dependent transport properties because the conductivity is proportional to the density of states at the Fermi level. If we assume the two sub-spin channels are completely separate in ferromagnetic metals, the two populations of electrons (spin-up and spin-down) will then carry the current in parallel with the majority of the current being carried by one spin or other (two current model). In practice, this assumption usually can be weakened by considering that the spin-flip scattering time $\tau_{sf}$ is much longer than any other relevant time scale in the problem. We will continue the discussion of this topic in the next section.
2.2 Magnetoresistance (MR)

Magnetoresistive effect is the property whereby some materials experience a change in their electrical resistance when an external magnetic field \( H \) is applied. Although the best way to describe this effect is by the function \( R(H) \), the numerical value of the relative resistance change is generally accepted as a way to characterize this effect. This numerical value is called magnetoresistance (MR) and defined as:

\[
MR = \frac{R(H) - R(0)}{R(0)}
\]

(2.4)

2.2.1 Anisotropic Magnetoresistance (AMR)

Anisotropic magnetoresistance (AMR) \([35]\) is an effect existing in any ferromagnetic metals, which shows that the resistance of ferromagnetic metals depends on the relative angle between the orientation of the sample’s magnetization and the direction of the electric current. AMR effect originates from the spin-orbital interaction and can be described by \([36]\):

\[
\rho = \rho_0 + \Delta \rho \cos^2 \theta
\]

where \( \rho_0 \) represents the film resistivity at zero magnetic field, \( \theta \) is the angle between the magnetization and current direction, and \( \Delta \rho \) is the total field-dependent change in resistivity. Figure 2.3 shows of a 100-nm-wide cobalt sample which exhibits an AMR effect of 1.8\% in a magnetic field of 8 kOe \([37]\). Of all the common magnetic materials, permalloy (Ni\textsubscript{70}Fe\textsubscript{21}) yields the largest useful magnetoresistance ratio (2 ~ 3\% with 100 Oe applied).
Giant Magnetoresistance (GMR)

Giant magnetoresistance (GMR) effect was first discovered in 1988 by Baibich et al. [2] and Grunberg et al. [3] in a (001)Fe/(001)Cr magnetic superlattice structure. They observed the sample resistance dropped to almost 50% by applying a strong magnetic field at low temperatures. The resistance change is more than an order of magnitude larger than that of the AMR effect, and thus was termed “giant” magnetoresistance. This discovery was responsible for the evolution of magnetoelectronics into a new and active field of condensed matter physics [9]. A GMR system is a perfect tool for reading data from hard disks when information registered magnetically has to be converted to electric current. This technology has made it possible to miniaturize hard disks so radically in recent years. Due to the significant impact the GMR effect made to our daily life, the 2007 Physics Nobel Prize was awarded to Albert Fert and Peter Grunberg each independently discovered the GMR effect [39].

Other than Fe/Cr superlattice structure, similar effects were soon observed in a wide variety of artificial thin-film materials composed of alternating ferromagnetic and...
nonmagnetic layers, such as the Co/Cu [40], Co/Ru, Co/Cr and Fe/Cu [41] systems, with MR values ranging between 30 ~ 80% [42].

The primary mechanism of GMR can be understood by considering the fact that the two spin channels of current (spin up and spin down electrons) have different scattering probabilities depending upon the magnetization of the layer they are traveling through. This is due to the difference in the density of empty states at the Fermi level [36]. If we adopt the aforementioned two current model (no interaction between spin-up and spin-down electrons), the electrical current passing through the structure can be taken as the sum of two separate spin channels and the overall resistance is given by the effective resistance of these two resistances in parallel. Figure 2.4 provides a schematic view of this two current model. For simplicity, this figure shows only a tri-layered structure instead of a multilayered one. If we assume the resistivities of spin-up and spin-down electrons are $\rho_\uparrow$ and $\rho_\downarrow$ respectively, the resistivity of the tri-layered structure with antiparallel magnetization configuration can be written as:

$$\rho_{AP} = \frac{1}{2} \left( \frac{\rho_\uparrow}{2} + \frac{\rho_\downarrow}{2} \right)^{-1} = \frac{\rho_\uparrow + \rho_\downarrow}{4}$$

If the tri-layered structure is in the parallel magnetization configuration, this resistivity then becomes:

$$\rho_P = \frac{1}{\rho_\uparrow^{-1} + \rho_\downarrow^{-1}} = \frac{\rho_\uparrow \rho_\downarrow}{\rho_\uparrow + \rho_\downarrow}$$
The GMR value, defined as the difference between these two extreme resistances divided by the resistance in the parallel state, is given by:

\[
GMR = \frac{R_{AP} - R_P}{R_P} = \frac{(\rho_\uparrow - \rho_\downarrow)^2}{4\rho_\uparrow\rho_\downarrow} = \frac{(\alpha - 1)^2}{4\alpha}
\]

where \( \alpha = \rho_\uparrow/\rho_\downarrow \) is defined as the spin asymmetric ratio.

The above simple two current model neglects the spin-flipping scattering due to magnons, which is unavoidable at high temperatures. Thus, when increasing temperature, the decreased \( \alpha \) will result in a decreased GMR value. Furthermore, we have assumed that the current is perpendicular to the plane (CPP) of the trilayered structure, however, GMR
effect is also observed in the current-in-plane configuration but with a smaller MR. Finally, the low resistance (usually in nΩ range) inherent to the CPP geometry make the measurements and practical applications very difficult [43].

### 2.2.3 Tunneling Magnetoresistance (TMR)

In 1995, Moodera [4] at MIT and Miyazaki [44] at Tohoku University independently discovered a large magnetoresistance effect (up to 11% at room temperature) in a multilayered structure, which consists of two ferromagnetic electrodes separated by a very thin insulating layer (~ several angstroms). This FM/I/FM structure is called magnetic tunneling junction (MTJ), which attracted huge amount of experimental and theoretical work done in the last decade due to the rich physics behind this phenomena (quantum tunneling) and potential applications in the areas of non-volatile random access memory (MRAM) and next-generation of magnetic sensing devices [9,45].

In an MTJ structure, the tunneling current through the thin insulating layer depends on the relative magnetization orientations of the two ferromagnetic electrodes, which means the resistance of the MTJ structure can be altered using external magnetic field. This new MR effect is referred to as tunneling magnetoresistance (TMR), and the first TMR experimental result is shown in Figure 2.5.
Since tunneling electrons are distributed around the Fermi level $E_F$, the tunneling probability of each channel is proportional to the product of the density of states of the two electrodes at their respective Fermi level. Thus, we have:

$$T_{\eta(\downarrow)} \propto D_\uparrow(E_{F1})_{\eta(\uparrow)} D_\downarrow(E_{F2})_{\eta(\downarrow)}$$

If the magnetizations of two ferromagnetic layers are parallel, shown in Figure 2.6, the spin-up (down) electrons in the first electrode tunnel to the available spin-up (down) states in the second electrode. Based on the two current model, the tunneling probability of this FM/I/FM system can be estimated as:

$$T_{\uparrow\uparrow(P)} \propto D_{\uparrow\uparrow} + D_{\uparrow\downarrow}D_{\downarrow\downarrow}$$
However, when the magnetizations of two ferromagnetic layers are in antiparallel configuration, the spin-up (down) electrons can only tunnel to the spin-down (up) states, therefore the resistivity of this system then becomes:

\[ T_{↑↓(AP)} \propto D_{1↑}D_{2↓} + D_{1↓}D_{2↑} \]

Since the conductivity \( \sigma \) is proportional to the tunneling probability \( T \), the TMR value, defined as the total change in resistance between these two extreme states, normalized to the parallel state resistance, is given by:

\[
TMR = \frac{R_{AP} - R_P}{R_P} = \frac{\sigma_{↑↑} - \sigma_{↑↓}}{\sigma_{↑↓}} = \frac{(D_{1↑} - D_{1↓})(D_{2↑} - D_{2↓})}{D_{1↑}D_{2↓} + D_{1↓}D_{2↑}} = \frac{2P_1P_2}{1 - P_1P_2} \ldots (2.6)
\]

with \( P_1 \) and \( P_2 \) being the spin-polarization of the two FM electrodes.

The above formula is a simplified model since it ignores the spin-flipping scattering, and also neglects the barrier contribution to the scattering. Still, it gives a good estimation of the maximal achievable MR (20 - 70% for conventional 3d ferromagnets) and
has been verified through many experiments. More importantly, it is evident in Equation (2.6) that the MR value is highly dependent on the magnitude of the spin polarization. Materials with small spin polarization value can only yield a low MR value, while an infinitely large TMR effect can be achieved in an MTJ structure with two fully spin-polarized ferromagnetic electrodes, which will be discussed in the next section.

Within almost ten years after the discovery of TMR effect, aluminum oxide (Al₂O₃) has been the most widely used tunneling barrier. Thin layers of Al₂O₃ are amorphous and consequently the TMR is mainly determined by the spin polarization of the two FM electrodes. However, it has been shown in 2004 that a much higher TMR (up to 200% at RT [5,46]) value can be obtained with epitaxial (001)-MgO being the tunnel barrier, which has been attributed to the spin dependent tunneling matrix of the single crystal MgO.

### 2.3 Half-metallic Ferromagnets

#### 2.3.1 Introduction

When discussing the tunneling magnetoresistance, we find that the highest MR value (nearly infinite) can be achieved with ferromagnetic materials having 100% spin polarization. This type of materials is called half-metallic ferromagnets, which has a Fermi surface in one spin channel, but for the opposite spin there is a gap in the spin-polarized density of states. The gap may occur in either the majority or minority channel [36].

Figure 2.7 shows the schematic diagram of a normal metal, a ferromagnetic metal and a half-metal. Normal metals, like copper and aluminum, have equal number of spin-up
and spin-down electrons at the Fermi level. Conventional ferromagnets such as Fe, Co and Ni are not half-metals. Regardless of the strongly spin-polarized $d$ band in those $3d$ ferromagnets, the conduction electrons are not fully spin polarized because of the presence of $4s$ electrons at the Fermi level. In order to obtain only spin-up or spin-down electrons at the Fermi level, reordering the $3d$ and $4s$ band is required, which is down by hybridization, pushing the bottom of the $4s$ band up above the $E_F$ or suppressing the $E_F$ in the $d$ band below the bottom of the $4s$ band. Therefore, all half-metals consist of more than one element, i.e. alloys or compounds [36].

![Density of States Diagrams](image)

Figure 2.7. Schematic diagrams for the densities of states of (a) normal metal, (b) ferromagnetic metal and (c) half-metal.

Usually people rely on the electronic band structure calculation to identify half-metals, because half-metallicity is not an easy property to measure experimentally, unlike normal metals, semiconductors or insulators where a distinct indication exists in
electrical transport. The response of a half-metal to an electric and magnetic field is quite different. It has electric conductivity but no high-field magnetic susceptibility. The application of an external magnetic field only shifts the spin-up and spin-down bands with no change in the net spin moment. Thus, the spin susceptibility becomes zero, like an insulator. Currently, the best indication of a half-metal is the integral number of Bohr magnetons per unit cell. A stoichiometric half metal has an integral number of electrons per formula unit \( n = n_\uparrow + n_\downarrow \), and an integral number in the spin-up (or spin-down) band because there is a gap with no spin-up (or spin-down) electrons at the Fermi level. Therefore, the number of spin-down (or spin-up) electrons is an integral number and so is the difference between them \( (n_\uparrow - n_\downarrow) \). Hence, the spin moment is an integral number of Bohr magnetons. This is a necessary but not sufficient condition for half-metallicity [47].

The unusual property of half-metals can have significant implications for applications related to magnetism and spin electronics. Electrically conducting ferromagnetic materials, where the conduction electrons have a high mobility and a full spin-polarization, are desirable for realizing future thin-film spin electronics devices. Furthermore, half-metallic ferromagnetic electrodes can serve as ideal spin injectors and detectors since they can only carry current in one spin direction under moderate voltage.

### 2.3.2 How to Measure Spin-polarization

Currently, the most widely used techniques to measure spin polarization includes: point contact Andreev reflection, photoemission, magnetic tunneling junction and Tedrow Meservey method, with each being discussed in the following.
a) *Point Contact Andreev Reflection (PCAR).* This is a process happening when a current travels from a normal metal to a superconductor through a point contact, shown in Figure 2.8(a). Since a Cooper pair is needed when an electron passing from a normal metal into a superconductor, to achieve this, a spin-up electron from the normal metal will be accompanied by the injection of a spin-down hole from the superconductor back into the metal when the junction is biased within the superconducting gap. If we replace the normal metal with a half-metal, no such electrons with opposite spin can be found to form the Cooper pairs. Thus for a half-metallic ferromagnets, the current is zero [11]. Normal metals and half-metals are two extreme cases, and the real effect depends on the degree of spin polarization. At absolute zero temperature, the spin polarization $P$ is given by:

$$P = 1 - \frac{G_0}{2G_n}$$

where $G_0$ is the conductance at zero bias voltage and $G_n$ is the conductance at high bias.

![Andreev Reflection](image)

Figure 2.8. (a) Schematic image of using PCAR method to measure spin polarization, and (b) normalized conductance $G(V)/G_n$ versus bias voltage $V$ for CrO$_2$/Pb point contacts at 1.2 K. The solid line is the best fit to the data. (taken from Ref. [6])
voltage (much larger than the superconducting gap). This technique is easy to implement since there is no limits on the sample geometry and no special surface preparation is required.

\textit{b) Magnetic Tunneling Junctions (MTJs).} MTJs are usually made up of thin film type of ferromagnetic electrodes separated by a thin layer of insulating oxide barrier, as shown in Figure 2.9. The quality of the insulating layer is the most important part the junction. So far, Al\(_2\)O\(_3\) is the most commonly used tunnel barrier material since it is amorphous, and thus the TMR value is mainly determined by the spin polarization of the ferromagnetic electrodes. The magnitude of the TMR can be expressed by:

\[
TMR = \frac{2P_1P_2}{1 - P_1P_2}
\]

where \(P\) is the spin polarization of the ferromagnetic electrodes. During experiment, the shape of the electrodes (usually thickness) can be controlled to yield different switching field, and the TMR value can be determined from the difference in resistance between the parallel and antiparallel states.

\textit{c) Spin-resolved Photoemission Spectroscopy.} Spin-resolved photoemission directly measures the half-metallicity of materials [48]. For majority spin channel, the photoemission spectrum will give a metallic Fermi cutoff, while for the minority spin channel it will give an insulating gap. The spin polarization of ejected photoelectrons can be measured for different incident photon energies. This method provides a direct image of the spin polarization near the Fermi level, however, it requires very careful surface preparation because the surface states have a critical influence on the final results.
Tedrow-Meservey Method. In 1994, Meservey and Tedrow measured the conduction electron spin polarization of magnetic materials using the Zeeman-split quasiparticle density of states in a superconductor [29]. This technique, shown in Figure 2.10(a), involves a tunnel barrier and a thin layer of superconducting aluminum as the second electrode, which serves as an analyzer of the spin polarization of the tunneling current. Their results show that the conduction electrons in ferromagnetic metals are spin polarized and the spin is conserved during the tunneling process. The normal tunneling behavior from a ferromagnet into a superconductor in zero field in shown in Figure 2.10(b). It depends on the convolution of the ferromagnetic and superconducting densities of states, and the gap between the two peaks are just the superconducting gap. When external magnetic field is applied, the superconductor quasiparticle density of state are Zeeman split, which divides the tunneling current into spin-up and spin-down parts yielding a asymmetric curve as shown in this Figure. The spin polarization is usually inferred from the conductivity at the four points marked with $\sigma_i (i=1-4)$, using the following relation [49]:

\[ \sigma_i = \frac{I_i}{V} \]

where $I_i$ is the current at the $i$th point and $V$ is the voltage.
2.3.3 Half-metallic materials

In this section, we will describe some materials that are theoretically claimed to be half-metallic. These materials can be divided into two main categories – oxides and Heusler alloys. The oxide category contains CrO$_2$, Fe$_3$O$_4$, La$_{0.7}$Sr$_{0.3}$MnO$_3$ and Sr$_2$FeMoO$_6$, etc. The Heusler alloys consist of four interpenetrating fcc sublattices, some of which may or may not be filled. Half-Heusler alloy (shown in Figure 2.11(a)) has ABC composition with Clb crystal structure, and the A$_1$ sublattice is empty (such as NiMnSb and PtMnSb, etc.). Full-Heusler alloy (shown in Figure 2.11(b)) has A$_2$BC composition with L2$_1$ structure, and all the sublattices are filled (such as Co$_2$MnSi and Co$_2$Cr$_{0.8}$Fe$_{0.4}$Al, etc.). Table 2.3 summarizes the list of different types of half-metallic ferromagnets with Curie temperature and predicted spin moment per unit cell. Table 2.4 lists a number of mea-
measurements of spin polarization for half-metallic materials including conventional ferromagnets.

Figure 2.11. Crystalline structures of (a) half-Heusler alloys and (b) full-Heusler alloys.

<table>
<thead>
<tr>
<th>Category</th>
<th>Half-metals (predicted)</th>
<th>Curie Temperature (K)</th>
<th>Magnetic Moment (µB)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxides</strong></td>
<td>CrO₂</td>
<td>396</td>
<td>2</td>
<td>[18,50]</td>
</tr>
<tr>
<td></td>
<td>Fe₃O₄</td>
<td>860</td>
<td>4</td>
<td>[51,52]</td>
</tr>
<tr>
<td></td>
<td>La₀.₇Sr₀.₃MnO₃</td>
<td>390</td>
<td>&lt; 3.7</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Sr₂FeMoO₆</td>
<td>420</td>
<td>4</td>
<td>[53]</td>
</tr>
<tr>
<td><strong>Full-Heusler</strong></td>
<td>Co₂MnSi</td>
<td>985</td>
<td>5</td>
<td>[32,54]</td>
</tr>
<tr>
<td><strong>Alloys</strong></td>
<td>Co₂(Cr₀.₆Fe₀.₄)Al</td>
<td>690</td>
<td>&lt; 3.7</td>
<td>[55,56]</td>
</tr>
<tr>
<td></td>
<td>Mn₂VAl</td>
<td>760</td>
<td>2</td>
<td>[57]</td>
</tr>
<tr>
<td><strong>Half-Heusler</strong></td>
<td>NiMnSb</td>
<td>730</td>
<td>4</td>
<td>[32,58]</td>
</tr>
<tr>
<td><strong>Alloys</strong></td>
<td>PtMnSb</td>
<td>572</td>
<td>4</td>
<td>[58]</td>
</tr>
</tbody>
</table>

Table 2.3. Theoretically predicted half-metallic materials with corresponding Curie temperature and magnetic moments.
<table>
<thead>
<tr>
<th>Half-metals</th>
<th>Method</th>
<th>T (K)</th>
<th>SP (%)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>CrO2</td>
<td>Photoemission</td>
<td>300</td>
<td>95</td>
<td>[59]</td>
</tr>
<tr>
<td></td>
<td>PCAR</td>
<td>4.2</td>
<td>94 – 98</td>
<td>[11,6]</td>
</tr>
<tr>
<td></td>
<td>MTJ</td>
<td>4.2</td>
<td>8</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>Powder MR</td>
<td>4.2</td>
<td>82</td>
<td>[50,61]</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Photoemission</td>
<td>300</td>
<td>80</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>MTJ</td>
<td>4.2</td>
<td>43</td>
<td>[33,63]</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$MnO$_3$</td>
<td>Photoemission</td>
<td>40</td>
<td>100</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>PCAR</td>
<td>4.2</td>
<td>58 – 92</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>MTJ</td>
<td>4.2</td>
<td>85 – 95</td>
<td>[64,65]</td>
</tr>
<tr>
<td></td>
<td>Tedrow-Meservey</td>
<td>4.2</td>
<td>72</td>
<td>[66]</td>
</tr>
<tr>
<td>Sr$_2$FeMoO$_6$</td>
<td>MTJ</td>
<td>4.2</td>
<td>90</td>
<td>[67]</td>
</tr>
<tr>
<td>Co$_2$MnSi</td>
<td>MTJ</td>
<td>10</td>
<td>61</td>
<td>[68,69]</td>
</tr>
<tr>
<td></td>
<td>PCAR</td>
<td>300</td>
<td>20</td>
<td>[70]</td>
</tr>
<tr>
<td>Co$<em>2$(Cr$</em>{0.6}$Fe$_{0.4}$)Al</td>
<td>MTJ</td>
<td>300</td>
<td>42 – 47</td>
<td>[71]</td>
</tr>
<tr>
<td>NiMnSb</td>
<td>Photoemission</td>
<td>300</td>
<td>50 – 67</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>PCAR</td>
<td>4.2</td>
<td>58</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>MTJ</td>
<td>4.2</td>
<td>25</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>Tedrow-Meservey</td>
<td>0.4</td>
<td>28</td>
<td>[49]</td>
</tr>
<tr>
<td>Fe</td>
<td>PCAR</td>
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<td>43</td>
<td>[11]</td>
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<tr>
<td></td>
<td>Tedrow-Meservey</td>
<td>0.2</td>
<td>45 – 77</td>
<td>[73,5]</td>
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<tr>
<td>Co</td>
<td>PCAR</td>
<td>4.2</td>
<td>40</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>Tedrow-Meservey</td>
<td>0.2</td>
<td>42</td>
<td>[73]</td>
</tr>
<tr>
<td>Ni</td>
<td>PCAR</td>
<td>4.2</td>
<td>42</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>Tedrow-Meservey</td>
<td>0.2</td>
<td>31</td>
<td>[73]</td>
</tr>
</tbody>
</table>

Table 2.4. Experimentally measured spin polarization in various ferromagnets.
### 2.4 Properties of Bulk Chromium Dioxide

Chromium dioxide (CrO$_2$) is a ferromagnetic oxide which has been widely used as a particulate recording medium in storage applications. It crystallizes in the tetragonal rutile structure with lattice parameters of $a = b = 4.42$ Å and $c = 2.92$ Å, as shown in Figure 2.12(a). The formal electronic configuration is $(t^2_{2g})^1$ for Cr$^{4+}$ and $2p^6$ for O$^{2-}$ although there is some O$^{2-}$ to Cr$^{4+}$ charge transfer and strong mixing of oxygen hole and chromium electron states at $E_F$ [15,74]. Theoretical calculation of the electronic band structure, shown in Figure 2.12(b), indicates that CrO$_2$ is a half-metallic ferromagnet with 100% spin polarization of the conduction electrons, and a low-temperature magnetic moment corresponding to an integral moment of 2.0$\mu_B$ per unit cell. This prediction has been validated by several experimental observations, such as point contact Andreev reflection [11,6], the Tedrow-Meservey tunneling technique [75] and spin-resolved photoelectron spectroscopy measurements [59,16], indicating a very high spin polarization (up to 98%).

![Figure 2.12. (a) Schematic image of the crystal structure of CrO$_2$, and (b) density of state for majority and minority spins in CrO$_2$ (taken from Ref. [15]).](image)
2.4.1 CrO\textsubscript{2} Thin Film Deposition

Based on the phase diagram, chromium dioxide is found to be a stable chromium oxide material only at very high oxygen partial pressure and over a limited temperature range [76]. The role of the pressure is to hold the oxygen in the crystal lattice against the forces of the chemical decomposition from CrO\textsubscript{2} to a much more stable state Cr\textsubscript{2}O\textsubscript{3}. People have tried all kinds of low-pressure deposition methods, like Molecular Beam Epitaxy [77], Magnetron Sputtering and Electron Beam Evaporation, to make CrO\textsubscript{2} thin films but all failed to get the correct chemical phase Cr\textsuperscript{4+}. Till now, the metal organic chemical vapor deposition (MOCVD) under atmospheric pressure produces chromium dioxide thin films with the best quality [78,79].

This deposition method takes place in a two-zone furnace with a reaction tube placed inside, as shown in Figure 2.13. In our lab, oxygen flow rate is controlled to be of ~150 sccm through the reaction tube from the first to the second zone at atmospheric pressure. The source material (precursor), usually powdered chromium trioxide (CrO\textsubscript{3}), is placed in the first zone (source region) within a quartz boat, which is held at 260°C. A substrate, usually rutile-phased titanium oxide (TiO\textsubscript{2}), is placed in the second zone (reaction zone) at 400°C. During the deposition, oxygen gas carries the sublimed CrO\textsubscript{3} precursor from the source region to the reaction zone where it decomposes on the substrate to form CrO\textsubscript{2} with the evolution of O\textsubscript{2}, i.e.

\[ 2CrO_3 \rightarrow 2CrO_2 + O_2 \]

The phase purity and morphology of the films was found to be dependent on the surface of the substrate, the source temperature and the oxygen flow rate [18]. Single-phase
films can be obtained at substrate temperature of 390 - 450 °C, with a source temperature of 260 -280°C. Among these factors, the substrate temperature is the most important one, which determines the deposition rate and is essential to the quality of the film.

The surface morphology of the epitaxial and polycrystalline CrO$_2$ films, scanned using atomic force microscopy, are shown in Figure 2.14. The exipitaxial film exhibits elongated-platelet-like features and has a surface roughness RMS value of about 40 Å. However, the film grown on the polycrystalline TiO$_2$ seed layer is polycrystalline with an average grain size of 500 Å and an RMS roughness of 400 Å.

We also developed a method for the selective-area growth of CrO$_2$ films [80]. This is based on our initial observation that CrO$_2$ grows readily on a clean TiO$_2$ surface, but not on amorphous SiO$_2$. The selective-area growth process has been employed to directly deposit patterned CrO$_2$ nanostructures, which will be discussed in Chapter 4.

Figure 2.13. A schematic diagram of using MOCVD process to grow CrO$_2$ thin film.
2.4.2 Magnetic Properties

The temperature dependence of the spontaneous magnetization $M_s(T)$ for a 4000 Å thick CrO$_2$ film is shown in Figure 2.15(a). The magnetization values are obtained after subtracting the small paramagnetic background contribution from the epitaxial TiO$_2$ substrate. The spontaneous magnetization curve against temperature is close to a Brillouin function at higher temperatures [81]. At low temperatures the curve follows the expression $M(T) = M(0)(1 - AT^n)$ with $A = 5 \times 10^{-5}$ K$^{-3/2}$ and $n = 1.5$, the value expected from Bloch’s law. A sharp magnetic transition can be observed for the film with a Curie temperature ($T_c$) of 393 K, and the value of the saturation magnetization $M(0)$ at low temperatures is determined to be nearly 650 emu/cm$^3$, corresponding closely to the theoretical moment of 2$\mu_B$ per Cr ion observed in the bulk.
Figure 2.15. (a) Spontaneous magnetization as a function of temperature for a thick CrO$_2$ film. Inset shows the linear dependence of the normalized magnetization as a function of $T^{3/2}$ as low temperatures (taken from Ref. [79]). (b) Magnetic hysteresis loops of thick CrO$_2$ film measured at 5 K along the [010] and [001] directions. Inset shows the low field response (taken from Ref. [78]).

Figure 2.15(b) shows the magnetic hysteresis loops at 5 K for an epitaxial (100)-CrO$_2$ thin film with field applied in the [001] and [010] directions. The magnetic easy axis is clearly along [001] ($c$ axis) with close to ideal 100% remanence, while [010] ($b$ axis) is the magnetic hard axis direction exhibiting reversible behavior. As seen in the bottom inset, the magnetization loop along the [001] direction is a square with a relatively low coercive field ($H_c$) of approximately 15 Oe at 5 K. From the magnetization data along the hard axis, the anisotropy field $H_K$ is determined to be around 1350 Oe at 5 K.

2.4.3 Electrical Properties

The resistivity $\rho$ as a function of temperature $T$ for the epitaxial and polycrystalline film grown on TiO$_2$ is shown in Figure 2.16. The resistivity of the epitaxial film clearly exhibits metallic behavior and is anisotropic in the plane, with a small change in slope around the Curie temperature ($T_c$). While the $\rho$ at room temperature along the $c$-axis direction is about 250 $\mu\Omega \cdot$cm and decreases to 2.15 $\mu\Omega \cdot$cm at 2 K, the $\rho$ along the $b$-axis is a
bit lower at room temperature (177 \( \mu \Omega \cdot \text{cm} \)) but decreases to a higher value of around 4 \( \mu \Omega \cdot \text{cm} \) at 2 K.

It has been found that the residual \( \rho \) at low temperatures is very sensitive to the structural disorder, since the resistivity of the polycrystalline film, plotted as a dotted curve in Figure 2.16, is significantly higher than the epitaxial film prepared under the same condition. The difference is particularly striking at low temperatures, where the grain boundary resistance dominates for the polycrystalline film. It has been reported that annealing the polycrystalline sample in air at a temperature as low as 400 K \([82]\), which is much below the decomposition temperature of CrO\(_2\), dramatically increases its resistance. On the other hand, no noticeable effect is observed on the resistance of the epitaxial film annealed under the same condition. This provides additional confirmation that grain boundaries are responsible for the increased resistance and that annealing can easily modify the stoichiometry of the grain boundary region \([78]\).

![Figure 2.16. Resistivity of CrO\(_2\) films grown on (100)-TiO\(_2\) and polycrystalline TiO\(_2\) substrate. The resistivity is measured with the current direction either along the c-axis or the b-axis for the epitaxial film, and in an arbitrary direction for polycrystalline film (taken from Ref. \([18]\)).](image-url)
Magnetotransport properties

Magnetotransport measurements of bulk CrO$_2$ samples in all kinds of forms, like compact powders [61,83], polycrystalline films [18,82] and epitaxial films [18,78], have been reported recently.

Magnetoresistance value as high as 40% at 4.2 K was observed in CrO$_2$ powder compacts by Coey, etc [83]. The MR decreases rapidly with increasing temperature, and finally becomes less than 1% at room temperature. Coey attributes this large MR effect to the low-temperature tunneling of the spin-polarized electrons across grain boundaries which is superseded by electron hopping without spin conservation at higher temperature. By mixing the ferromagnetic CrO$_2$ with insulating antiferromagnetic Cr$_2$O$_3$ powder, an increase of the resistivity by three orders of magnitude was observed with a substantial enhancement of MR from 29% to 50% at 5K, which is a strong support of the intergrain tunneling mechanism [61].

For polycrystalline CrO$_2$ films made by high-pressure thermal decomposition of CrO$_3$, similar behavior has been found. Hwang and Cheong [82] observed a negative MR of 10% at 5 K and 3 Tesla for the as-deposited CrO$_2$ samples, while subsequent post annealing of the sample significantly increases the resistivity and MR to about 24% at 5 K. The increase of MR in the post-annealing films has been attributed to the modification of the effective intergrain tunneling barrier due to the decomposition of CrO$_2$ into insulating Cr$_2$O$_3$ at the grain surface.

Gupta and Xiao et al. [18] studied the MR properties of the epitaxial (100)-CrO$_2$ films grown on (100)-TiO$_2$ substrates and found a positive MR up to 25% at 5 K and 4
Tesla in the transverse geometry with current parallel to the [001]-direction. This MR value has been attributed to the Lorentz force effect, which is related to the mean free path and crystalline properties of the single crystal CrO₂ films.

![Figure 2.17](image)

Figure 2.17. (a) Magnetization (○) and resistance (●) of a CrO₂ powder compact at 5 K. The inset shows the detail at low field (taken from Ref. [61]). (b) Longitudinal and transverse MR (0 - 40 kOe) of a 4000Å thick epitaxial CrO₂ film measured at 5 K (Ref. [18]).

### 2.5 Summary

In this chapter, we reviewed the basics of magnetism with emphasis on the concept of spin polarization and half-metallicity, which is explained from the density of states point of view. We also discussed major types of magnetoresistance, such as AMR, GMR and TMR. The introduction of half-metallic ferromagnets into these structures may enlarge the MR effect amazingly. Several candidates that have been theoretically predicted to be half-metals are reviewed with their most recent experimental results. Finally, some of the bulk physical properties of the only experimentally confirmed half-metal, chromium dioxide (CrO₂) thin films, are described.
Chapter 3

Magnetic Domain Wall Resistance and Spin Transfer Torque Effect

A rapid growth has been made in the last two decades with a significant increase in activity in the area of nanomagnetism and spin-dependent transport. Partly, this has been driven by the improvements in the technology available for thin film deposition and characterization, as well as the capability to pattern these films into nanoscale devices, and also due to the applications in the data storage industry where the size of each magnetic bit approaching few nanometer scale requires a detailed understanding and manipulation of nanostructured magnetic materials [1]. The core concept in this field - magnetic domain and domain wall are introduced in this Chapter with emphasis on their relation with different magnetic energy terms. Also, a relatively new phenomenon called spin transfer torque effect, which controls the motion of domain wall(s) using an electrical current instead of an external magnetic field, is discussed.
3.1 Magnetic domain walls

3.1.1 Origins of magnetic domains

The concept of magnetic domains was first introduced by Pierre Weiss [84] in order to explain some experimental facts about ferromagnets, such as their extremely high permeabilities (the application of a few Oe can fully saturate a piece of soft iron while the internal field, in the order of MOe, cannot saturate the material). Part of the answer developed by Weiss was the introduction of molecular field, a manifestation of the exchange interaction. The other part was the assumption that the sample was made up of various fully magnetized regions, called magnetic domains.

The presence of magnetic domains was first experimentally confirmed by Sixtus and Tonks [85] and Bitter [86] at 1930s. Later on, Landau and Lifschitz [87] proposed that the formation of magnetic domains is due to the system seeking a minimized the magnetostatic energy, and also calculated the domain wall profile. Later on, Kittel [88] and Hubert and Schäfer [89] reviewed the basic ideas of magnetic domains and extend theory from the magnetostatic energy only to several energy terms.

The physical basis of domain formation is the competition between the various energy terms that describe a magnetic object. The total energy ($E_{\text{total}}$) can be simply written as the sum of these terms [36]:

$$E_{\text{total}} = E_{\text{magnetostatic}} + E_{\text{Zeeman}} + E_{\text{exchange}} + E_{\text{anisotropy}}$$
In the above formula, **magnetostatic energy** \( (E_{\text{magnetostatic}}) \) arises mainly from having a discontinuity in the normal component of magnetization across an interface. It is a form of anisotropy due to sample shape (shape anisotropy) and is often uniaxial in symmetry:

\[
E_{\text{magnetostatic}} = -\frac{\mu_0}{2} \int H \cdot M \, dV \quad \text{..........................(3.1)}
\]

**Zeeman energy** \( (E_{\text{Zeeman}}) \) is the potential energy of a magnetic moment in an externally applied magnetic field and tends to align the spins with this field:

\[
E_{\text{Zeeman}} = -\int M \cdot \mathbf{B} \, dV \quad \text{.............................(3.2)}
\]

**Exchange energy** \( (E_{\text{exchange}}) \) expresses the energy cost of a change in the direction of magnetization. It tends to keep adjacent magnetic moments parallel to each other:

\[
E_{\text{exchange}} = \frac{A}{M_s^2} \int \left( \left\| \nabla M_x \right\|^2 + \left\| \nabla M_y \right\|^2 + \left\| \nabla M_z \right\|^2 \right) \, dV \quad \text{.........(3.3)}
\]

Finally, **magnetocrystalline anisotropy energy** \( (E_{\text{anisotropy}}) \) describes the preference for the magnetization to be oriented along certain crystallographic directions. It tends to aligns spins with the magnetic easy axis direction:

\[
E_{\text{anisotropy}} = \frac{K_1}{M_s^4} \int \left( M_x^2 M_y^2 + M_y^2 M_z^2 + M_z^2 M_x^2 \right) \, dV \quad \text{.........(3.4)}
\]

Since the magnitude of the magnetization \( (M_s) \) is fixed, the way to achieve minimum total energy is to vary its direction. To determine the overall lowest energy direction for magnetization, some compromise must be made between these energy terms. As a result, some spins will no longer point to their own optimal directions. Usually, a uniformly magnetized
state has a high magnetostatic energy (Figure 3.1(a)), which can be reduced by forming a non-uniform (Figure 3.1(b) and 3.1(c)) or even flux-closed (Figure 3.1(d)) magnetic state. The formation of domains continues until the decrease in magnetostatic energy is balanced by the exchange and anisotropy energy costs, with twists and deviations in the magnetic structure. If an external magnetic field is applied, Zeeman energy also plays a role which may be large enough to erase the domain state and produce a uniform saturated state.

Figure 3.1. Schematic illustration of the break up and formation of magnetic domains (a) single domain state with uniform magnetization, (b) two-domain state with reduced magnetostatic energy, (c) four-domain state with even lower magnetostatic energy, and (d) a flux-closure domain state with zero magnetostatic energy (taken from Ref. [90]).

### 3.1.2 Magnetic domain walls

Generally magnetic domains are separated by narrow regions where the magnetization rotates from the direction of one domain to the next, and these regions are called domain walls (DWs) [36]. A zero length abrupt domain wall (i.e. the magnetic moments are oriented 180 degree with respect to each other at the domain interface) costs energy due
to the exchange interaction that tends to align the magnetic moments. It is therefore energetically much more favorable to cant the magnetic moments gradually over the domain wall region. There exist mainly two kinds of domain walls that differ in the direction of canting. The one that is most commonly seen is the Bloch wall, however, in thinner films a Néel wall is often favored.

Bloch wall is often seen in bulk magnetic materials with no magnetic charge associated with the wall, as is shown in Figure 3.2. Although magnetization vector rotates, \( \nabla \cdot \vec{M} = 0 \) is satisfied everywhere including the wall. Thus, there is no stray field and no extra cost in the magnetostatic energy associated with the creation of the wall. Since the neighboring magnetic moments are no longer parallel to each other, there is an extra cost in the exchange energy term. In order to achieve a small magnetocrystalline energy, the magnetization within the domains prefer to align along the easy axis direction, which means that the magnetization must rotate through a hard direction.

![Bloch wall (rotation out of plane)](image)

Figure 3.2. A schematic diagram for a Bloch wall where the rotation of magnetic moments happen out of the film plane.
This picture is somewhat different for a thin-film-shaped sample. Generally, the magnetization inside the domains will lie in the film plane, however, to form a Bloch wall, the magnetization must rotate out of the film plane. This will lead to surface changes and extra cost in magnetostatic energy which increases as sample thickness decreases. To reduce this energy, the magnetic moments inside the wall may rotate in the place of the surface, as shown in Figure 3.3. Such a domain wall is called Nèel wall.

![Neel wall (rotation in plane)](image)

Figure 3.3. A schematic diagram for a Neel wall where the rotation of magnetic moments happens in the thin film plane.

### 3.1.3 Domain wall thickness

Suppose there are two semi-infinite domains separated by a domain wall which consists of $N$ planes of spins with lattice constant $a$ being the distance between neighboring planes, as shown in Figure 3.4. The magnetization rotates $180^\circ$ from one domain to the other. To further simplify the case, we assume each domain occupies one of the easy axes (uniaxial anisotropy).
Figure 3.4. Schematic of ferromagnetic material containing a $\pi$-domain wall with spins reverse direction spreading over $N$ atomic distances.

The adjacent spins will differ by an angle $\theta$ which is approximately $\theta \approx \pi/N$. With Heisenberg Hamiltonian, the exchange energy term associated with a pair of neighboring spins can be written as $-2J S^2 \cos(\pi/N)$. In real materials, $N$ is found to range from about 40 to nearly $10^4$ [36], thus the total exchange energy density can be approximated by:

$$E_{\text{exchange}} = -\frac{2NJS^2}{a^2} \cos\left(\frac{\pi}{N}\right) \approx -\frac{2NJS^2}{a^2} \left(1 - \frac{\pi^2}{2N^2}\right) = \frac{JS^2 \pi^2}{Na^2} + \text{const.}$$

The constant $-2NJS^2/a^2$ is the background energy density and can be neglected. We can see that $E_{\text{exchange}}$ is inversely proportional to $N$, in order to obtain a smaller exchange energy, the magnetic system tends to make $N$ as large as possible, which means the rotation will be as gradual as it can be.

One the other hand, the domains occupy the easy axis orientations so that the spins within the domain walls are in a hard axis direction. This increases the anisotropy energy per unit area by:

$$E_{\text{anisotropy}} = K_u \left(\frac{N}{a^2}\right)a^3 = K_u Na$$
where $K_u$ is the anisotropy constant. Since $E_{\text{anisotropy}}$ is proportional to $N$ (contrary to the exchange effect), the anisotropy effect wants to compress the domain wall to be as thin as possible, in order to align most of the spins in the easy axis direction.

Thus, the equilibrium domain wall thickness ($D = Na$) is the value which minimizes the total energy, i.e. the sum of the aforementioned two energy terms:

$$E_{\text{DW}}(N) = E_{\text{exchange}} + E_{\text{anisotropy}} = \frac{JS^2 \pi^2}{Na^2} + K_u Na \geq 2 \sqrt{\frac{JS^2 \pi^2 K_u}{a}} = 2\pi \sqrt{AK_u}$$

where $A=JS^2/a$ is the exchange stiffness constant. The critical $N$ that minimizes the total energy satisfies $N' = (\pi/a)\sqrt{A/K_u}$, hence the domain wall thickness $D=N'a$ is given by:

$$D = \pi \sqrt{A/K_u} \quad \text{...............................(3.5)}$$

And the domain wall energy per unit area is:

$$\sigma_{\text{DW}} = 2\pi \sqrt{AK_u} \quad \text{...............................(3.6)}$$

This is the energy cost of creation of a domain wall per unit area in terms of the exchange and anisotropy contributions only. Since the wall energy is proportional to the area of wall, the domain wall has a tendency to be as flat as possible. Although this is a simplified model, it yields a correct order of magnitude estimate for the domain wall thickness. For system with small anisotropy such as soft magnetic materials, $D$ is of the order 200 nm, while in high-anisotropy systems such as permanent magnets, $D$ can be as small as 10 nm.
3.1.4 Domain wall resistivity (DWR)

Early theoretical studies of the electronic properties of domain walls were stimulated by the magnetotransport experiments performed on single crystal Fe whiskers [91,92]. It was observed that a small magnetic field erased the domain walls from a multi-domain state and produce large reduction in resistivity by an order of magnitude at low temperatures. Later on the discovery of GMR effect [3,2], which is associated with magnetic domain reorientation in ferromagnetic multilayers, renewed the interest in the electronic properties of domain walls. In a GMR device, spin-dependent electron transport effects are expected to be important to understand the scattering of electron by DWs. It is only in the last few years this possibility has been studied in some detail theoretically.

The first model regarding DWR was raised by Cabrera and Falicov [93], who assumed that the electrons travelling in one domain would experience a different potential when entering an oppositely magnetized domain since the band minimum differs by the exchange energy splitting. They calculated the reflection coefficients of the electron wave function at the potential steps and found the magnetoresistance of the domain wall $\Delta \rho/\rho$ was proportional to $\exp(-\pi D k_F)$, where $D$ is the domain wall thickness and $k_F$ is the Fermi wave vector. However, $D$ is generally more than one order of magnitude larger than Fermi wavelength $2\pi/k_F$, thus the predicted magnetoresistance ($< 0.01\%$) and DWR is entirely negligible, which is contradictory to the experimental results.

In recent models, the most essential ingredients are the spin-dependent potentials and scattering rates, i.e. the potentials and electron relaxation times are different for spin-up and spin-down electrons in ferromagnets. Compare with the aforementioned electron reflection from a DW, these models significantly amplify the effect of domain
wall on the conductivity and produce results that is closer to the experimental results. The basic idea is the two-current model, which is explained in the following [94]. In a uniformly magnetized domain, a large fraction of the total current is carried by one spin channel (spin-up or spin-down). When electrons pass through the domain wall, there is mixing of the spin channels within the DW, due to a small non-adiabaticity of the electron spins. It is this mixing that increases the resistivity of the DW region.

Levy and Zhang [94] evaluated this additional resistivity using semiclassical Boltzmann calculation for a simplified one-dimensional DW structure, and found two useful formulas for two basic measurement geometries: CPW (current flow normal to the domain wall) and CIW (current flow in the domain wall place). The two corresponding magnetoresistance can be written as:

$$MR_{\text{CPW}} = \frac{\xi^2}{5} \left( \frac{\rho_\uparrow - \rho_\downarrow}{\rho_\uparrow \rho_\downarrow} \right) \left( 3 + \frac{10 \sqrt{\rho_\uparrow \rho_\downarrow}}{\rho_\uparrow + \rho_\downarrow} \right)$$

$$MR_{\text{CIW}} = \frac{\xi^2}{5} \left( \frac{\rho_\uparrow - \rho_\downarrow}{\rho_\uparrow \rho_\downarrow} \right)$$

where the leading coefficient $\xi$ is the spin-mixing parameter and represents a measure of the non-adiabaticity, $k_F$ is the Fermi wave vector, $D$ is the domain wall width, $J$ is the exchange energy splitting and $\rho_{\uparrow(\downarrow)}$ is the resistivity of the spin-up (down) channel. The magnetically saturated resistivity ($\rho$) of the ferromagnet is calculated by $1/\rho = 1/\rho_\uparrow + 1/\rho_\downarrow$. It can be seen that after some manipulations the above formula actually depend only on the spin-asymmetry ratio $\alpha = \rho_\uparrow/\rho_\downarrow$ and $\xi$ [95]. For typically parameters for cobalt, $k_F = 10$ nm$^{-1}$, $J = 0.5$ eV, $D = 15$ nm and $\rho_\uparrow/\rho_\downarrow = 5$, the CPW-MR is estimated to be nearly 2% which is close to the experimental results. Note that this is the MR value of the DW material itself.
In real experiments, the contribution from domains is often inevitable, which will result in a reduction of the measured MR by a factor determined by the DW thickness and the domain size.

In Levy and Zhang’s model, the MR ratio within the wall is inversely proportional to the square of the DW thickness, so that narrow domain walls are necessary to obtain a large MR value. Similar results have also been obtained when the ballistic or diffusion transport through a domain wall is taken into consideration [96,97]. Furthermore, the MR ratio is independent of the overall scattering rate, instead it is the spin-polarization of the current that determines the size of this effect. One can expect a huge DWR value for a half-metallic material since the spin-asymmetry ratio $\alpha$ is close to infinite for half-metals [98]. This also stimulates our interest in studying the domain wall properties of half-metallic CrO$_2$, the details of which will be discussed in the following Chapters.

Finally, it is important to note that Levy and Zhang’s model is a perturbative result, and thus the above formula is not valid in the limit of a very narrow domain wall thickness, such as an atomic scale DW. In this case the electron reflection would indeed be significant and MR effects can be greatly amplified [99].

Not all theories predict the presence of a positive domain wall contribution to the resistivity. For instance, Tatara and Fukuyama [96] presents that the spatially inhomogeneous magnetization within the domain wall can contribute to the decoherence of the electrons, reducing the quantum contributions to the resistance. As a consequence, erasing domain wall(s) with external magnetic field restores the coherence and leads to an increase in the resistivity.
3.2 Nanomagnetism

The study of the magnetic properties of nanostructured ferromagnets has been a very active research field in recent years [20]. One of the reasons is that applications in high density magnetic recording and spintronics require element dimensions reduced down to the nanometer scale [100]. Also, for these small structures, interesting changes in the magnetic behavior are expected, as the sample size becomes comparable to characteristic length scales in the material such as the domain wall width [101]. Furthermore, recent advances in the nanofabrication technology [102,103] enable us to precisely control the geometrical factors in the nanometer scale, which govern the configuration of domain structure. Therefore, in these nano-sized samples magnetic properties can be strongly modified in comparison to continuous films or bulk material.

As we have mentioned in the previous section, magnetic properties of certain magnetic objects depend on the balance of the exchange energy, the magnetic anisotropy energy (magnetocrystalline, shape, etc.) and the demagnetizing field. In order to decrease the demagnetizing fields (magnetostatic energy), magnetic domains may be formed in bulk materials [36]. However, as we decrease the geometrical size of the object, the formation of domains varies significantly, which is related with two critical length scales [1].

The first length scale, called critical single domain radius, is the size at which the presence of a domain wall in the material is energetically favorable [104]. This value is different for various nanostructured materials since the domain wall energy is determined by the anisotropy constant ($K_u$) of the material. For instance, the single domain radius for special epitaxial nanoparticles is 6 nm for iron, 34 nm for cobalt but 764 nm for SmCo$_5$. 
However, this critical radius can be much smaller for polycrystalline nanostructured samples due to the reduction in the magnetocrystalline anisotropy.

The second critical length scale is the domain wall thickness $D$. For magnetic nanostructures, it is obvious that domain wall(s) cannot exist if the size of the nanostructure is comparable to the domain wall thickness. Therefore, magnetic nanostructures with size smaller than $D$ remain in a single-domain state. However, single-domain state does not necessarily mean a uniformly magnetized region, but a state without the presence of domain wall(s) such as the flux-closure states discovered in magnetic nanodots [20].

When the size of the object decreases, shape anisotropy becomes much more significant since it is one of the most important aspects determining the magnetic state of nanostructures, especially for samples with small magnetocrystalline anisotropy such as polycrystalline nanostructures [36]. In these cases, shape anisotropy dominates the magnetic behavior of the system. For example, polycrystalline ferromagnetic rectangular or elliptical blocks have a strong tendency to align the easy axis along the wire direction [105]. Finally, due to the high surface-to-volume ratio, the surface anisotropy could also be important for magnetic nanostructures through the introduction of spin disorder [106,107].

In following, we briefly discuss the basic properties of some typical nanostructured magnetic elements including nanodots, nanowires and nanorings.

### 3.2.1 Magnetic Nanodots

For large-sized dots, domains are formed to minimize the external magnetic flux and the demagnetizing field. If the size of the nanodot is sufficiently small, a single-domain
state (without DW) can be formed at remanence, such as the flower state (nonzero net magnetization) or the vortex state (zero net magnetization), as shown in Figure 3.5(c).

The vortex state [108,109] forms a closed magnetic flux circuit by having a continuous twisting of the magnetization in the plane of the wafer, which represents the attempt to lower the magnetostatic energy at the cost of creating non-collinear magnetization.

![Figure 3.5. Hysteresis loop of a magnetic nanodot array with the micromagnetic simulations representing the spin configurations of the dot array along the path of the hysteresis loop.](image)

Figure 3.5. Hysteresis loop of a magnetic nanodot array with the micromagnetic simulations representing the spin configurations of the dot array along the path of the hysteresis loop. (a) Spin configuration aligned with the field direction; (b) at the point of nucleation of the vortex core at the right edge of the dot; (c) the symmetric vortex in zero field; (d) the vortex core, as it shifts to the left with increasing applied field, but before being annihilated at the left edge of the dot; and (e) the reverse of (a) (taken from Ref. [20]).
arrangements within a single-domain ferromagnet. Because the twisting of the magnetization becomes too severe at the core of the structure, the spin structure develops a singularity over a lateral length scale of order 10 nm where the magnetization progressively cants and points out of the plane of the wafer. The typical in-plane magnetization process of a magnetic nanodot is shown in Figure 3.5, with the micromagnetic simulations displayed at the lower part. The non-hysteretic part of the magnetization loop is associated with the vortex core moving to the left (Figure 3.5(d)) or right, depending on the direction of the external magnetic field. The hysteretic part is associated with the creation or annihilation of vortex at the edge of the dot.

Many magnetic properties are quite different between magnetic dots and its corresponding continuous films because of the different domain structures. Generally, single-domain nanodots have larger coercive field \( H_c \) due to the change in reversal mechanism from domain nucleation to coherent rotation \([110,111]\). Also, the remnant magnetization reduces due to the formation of closure-domains \([112]\). In other word, the whole magnetization process, i.e., the hysteresis loops, of nanodots are drastically different from bulk materials, as evidenced in Figure 3.5.

Finally, for magnetic dots with volume \( V \), the anisotropy energy \( K_u V \) may becomes comparable or even smaller than the thermal activation energy \( k_B T \). As a consequence, the thermal fluctuations are large enough to overcome the energy barriers that separate the different spin states within the time frame of the measurement, hence the magnetic dots will be no longer ferromagnetic \([105,1]\). However, at lower temperature (smaller thermal energy) they may become ferromagnetic again \([113]\).
3.2.2 Magnetic Nanowires

For magnetic nanowires made by polycrystalline ferromagnets or materials with weak magnetocrystalline anisotropy, the dominant shape anisotropy, due to the high aspect ratio, aligns the magnetic easy axis parallel to the wire axis, resulting in a relatively simple and controllable domain structure. On the other hand, contrary to magnetic nanodots, the magnetic properties of nanowires can be indirectly measured through the conventional magnetotransport measurement \[114\]. Therefore, the magnetic nanowires (including straight lines, constrictions, zigzags \[115\] and modified ends \[116\]) are the most widely accepted geometry to study the interaction of electronic transport with domain structures.

Generally, when decreasing the width of the wire, the coercivity \(H_c\) in the longitudinal direction (parallel to the wire) increases \[117\]. This is due to the existence of magnetic ripple structure in nanowires, which causes domains with magnetization perpendicular to the line and blocks the domain propagation along the line during the reversal process \[118\]. The saturation field in the perpendicular direction also increases with decreasing linewidth \[117\], which is a direct consequence of shape anisotropy. The saturation field can be estimated by \(H_s = (3/2)H_{Demag} = (3/2)(t/w)M_s\), where \(H_{Demag}\) is the demagnetizing field of the wire and \(t\) and \(w\) are the thickness and linewidth of the wire \[119\]. Thus, for a fixed thickness, the saturating field will be inversely proportional to the width of the wire.

However, for single crystal nanowires, the shape anisotropy are no longer the only dominant term since the magnetocrystalline anisotropy cannot be neglected. As a result, the magnetic behavior is determined by several factors, leading to an increasingly com-
plicated reversal mechanism. For instance, a transition from positive to negative anisotropic MR has been discovered with temperature in epitaxial cobalt nanowires [120].

Recently, an active area of research in the field of magnetic nanowires emerges, which studies the control and manipulation of domain wall(s) by changing the shape of the wires. For example, it has been found that a constricted nanowire can pin domain(s) or domain wall(s) at the tip area, which can be removed by a sufficiently large spin-polarized current and result in a pronounced drop in resistance [121, 24]. We utilized this property and studied the domain wall resistivity of half-metallic chromium dioxide nanocontact structures, which is discussed in Chapter 8.

3.2.3 Magnetic Nanorings

The ring geometry has good potential for use in high density data storage and bio-detection due to its relatively simple magnetic switching process [122]. Usually, a magnetic nanoring has two stable states: vortex state and onion state [123].

For samples with weak magnetocrystalline anisotropy, the lowest energy state for a magnetic ring at remanent state, is the flux-closure vortex state, as shown in Figure 3.6. The magnetic moments chase one another in a circle, resulting in zero magnetostatic energy and keeping the exchange energy low with gradual magnetic moment direction changes. When an increasing magnetic field is applied, the magnetic ring will enter the onion state characterized by the presence of two opposite head-to-head domain walls. This maintains the low exchange energy properties of the vortex state (except at the bottom and top of the ring, where the magnetic moments point in opposite directions) while allowing
some magnetization in the direction of the applied field. Thus two transitions occur when decreasing the magnetic field: first the nanorings switch from the onion state (d) to the vortex state (c) and later they switch from the vortex state (c) to the opposite onion state (b), as shown in the hysteresis loop in Figure 3.6.

Other than the Magneto-optical Kerr effect (MOKE) and magnetic force microscopy (MFM) techniques, the magnetic properties of nanorings can also be studied using magnetotransport measurements [124,125].

Figure 3.6. MOKE measurement showing double switching for nanorings with 110 nm outer diameter. (a and c) are vortex states and (b and d) are onion states with the position of domain walls indicated with vertical lines (taken from Ref. [126]).
### 3.4 Spin angular momentum transfer

It is well known that the configuration of magnetization orientation in a ferromagnetic system affects the electrical transport properties of the system. For example, the resistance of a GMR structure depends on the relative magnetization orientation of individual ferromagnetic layers (parallel or antiparallel states). On the other hand, the so-called spin angular momentum transfer (spin-transfer) refers to the reverse effect, which means the influence of a spin-polarized current on the magnetization state of a ferromagnet. Although this effect was first discovered in the 1980s [127, 128], only recently due to the availability of nanofabrication techniques and its possible applications in magnetic random access memory (MRAM) [129, 130], there is a resurgence in this field. This can be partly attributed to the experimental fact that spin-transfer effect can be observed only in magnetic structures with size smaller than 100 nm [8, 131].

Spin-transfer effect originates from the exchange of angular momentum between the spin-polarized current and the magnetization and its basic concept is shown in Figure 3.7. First the current passes through the left ferromagnet (F1) and become spin-polarized, then when it passes through the second, a much thinner FM layer (F2), the polarization direction of the current has to change to match that of the second layer (F2). As the spins in the conduction current relax into this new direction, there is a change in the angular momentum by ħ for each spin that flips. This continuous change of angular momentum corresponds to a torque ħPJ/e exerted on the second FM2 layer. If this torque is large enough to overcome the anisotropy barrier of the FM2 layer, then its magnetization can be switched to match the incoming current. Reversing the current will reverse the sign of the torque and switches the layer back.
Slonczewski calculated the torque caused by a charge current $I$ on a macrospin $S_i$, representing the moment of one of the two ferromagnetic layers and found the transverse component of the spin-torque is given by \[ S_{1,2} = g(s_1 \cdot s_2, P)I \frac{1}{e} s_{1,2} \times (s_1 \times s_2) \] where $s_1$ and $s_2$ are the unit vectors in the directions of the two macrospin and $g$ is a factor dependent on the current spin polarization $P$ and the inner product $s_1 \cdot s_2$. It is obvious that the torque is proportional to the current flow and will change sign when the current does.

Later, Sun considered the injection of a spin-polarized current into a single domain nanomagnet using modified Landau-Lifshitz-Gilbert equation and found out the magnitude of the critical spin-injection current is \[ I_c = \left( \frac{2e}{h} \right) \left( \frac{\alpha}{P} \right) VM_s \left( H + H_k + 2\pi M_s \right) \]
where $M_s$ is the saturation magnetization, $V$ is the volume of the nanomagnet, $\alpha$ is the Gilbert damping coefficient, $H_k$ is the anisotropy field and $H$ is the external magnetic field. Typically, a current density as high as $10^{11} \sim 10^{13} \text{ A/m}^2$ is required to allow the switch happen, and this is the reason why spin-transfer effect can only be seen in very small magnetic structures.

One of the most promising applications of spin-transfer torque effect is to write data in a magnetic random access memory using electrical current instead of a magnetic field. The use of external magnetic fields to switch magnetic bit can cause several problems such as crosstalk and high power consumption. However, driving the currents through each magnetic element is an energetically much more efficient way, and it also eliminates the possibility of crosstalk. From application point of view, a critical current density $J_c$ as low as $10^8 \text{ A/m}^2$ is a must. In order to lower this value, ferromagnets with high spin polarization and low damping coefficient is preferable.

### 3.4 Summary

In this Chapter, we described the origin of magnetic domains and domain walls, which is the direct consequence of the competition between different magnetic energies. Theoretical results regarding the properties of domain wall thickness and resistivity are briefly reviewed. On the other hand, the interesting physics, emerging when the geometrical dimension of the ferromagnets are reduced down to sub-100 nm (such as nanodots, nanowires and nanorings), are introduced. Finally, a relatively new phenomenon called spin transfer torque effect is described in order to provide the background knowledge to understand the experimental work of Chapter 8.
Chapter 4

Experimental Techniques

The principal experimental methods and techniques used by the author for the completion of his Ph.D. thesis are described in this chapter, which include thin film deposition techniques (MOCVD, EBE and magnetron sputtering); optical and electron-beam lithography; etching methods (wet etching, RIE and Ion beam etching), characterization methods (XRD, SEM, AFM & MFM, VSM), and low temperature electrical measurement systems (liquid nitrogen cryostat and cryogen free closed-cycle refrigerator).
4.1 Thin Film Deposition

In recent years, thin film science has grown world-wide into a major research area. The importance of coatings and the synthesis of new materials for industry have resulted in a tremendous increase of innovative thin film deposition technologies. All deposition method can be classified as either a chemical vapor deposition (CVD) or a physical vapor deposition (PVD). CVD processes involve the creation of a vapor phase of the deposited material through a chemical reaction, while PVD is a deposition method that are used to release a material from a source and transfer that material to a substrate, forming a thin film or coating. PVD processes are commonly used for the deposition of metals because they can be performed at lower process risk and cheaper in regards to materials cost than CVD.

4.1.1 Metal Organic Chemical Vapor Deposition (MOCVD)

Metal Organic Chemical Vapor Deposition (MOCVD) is a technique widely used in the growth of epitaxial metal oxides and semiconductor compounds. Usually, this system has two zones at different temperatures, with the low temperature zone for evaporating metal organic precursors (CrO$_3$ [18,26], Ru(TMHD)$_3$ [134] etc.), and the high temperature zone for the actual depositions on the substrates. An inert gas is normally used for carrying the gas phase precursor to the substrates for decomposition, and in some cases a reactive carrier gas can also be used to serve as a reagent (as in RuO$_2$ depositions).

We use this technique for the deposition of epitaxial rutile-phased chromium dioxide (CrO$_2$) heterostructures in our lab, as shown in Figure 4.1. The details will be discussed in the next Chapter. In brief, oxygen is used as a carried gas between two furnaces.
to transport the sublimed chromium trioxide (CrO$_3$) precursor from the source region (T = 280°C) to the reaction zone (T = 400°C) where it decomposes onto the surface of TiO$_2$ substrate and form CrO$_2$ thin film with the evolution of O$_2$.

![Figure 4.1. Schematic drawing of the MOCVD system for CrO$_2$ deposition.](image)

### 4.1.2 Thermal Evaporation and Electron Beam Evaporation

Unlike the aforementioned MOCVD, depositing material using evaporation is a PVD process. Thermal evaporation is by far the most widely used method to make thin films. In this process (shown in Figure 4.2(a)), the source materials, usually metals, is heated in a vacuum chamber until it starts to boil and evaporate. The vapor then condenses on the surfaces inside the chamber with any object exposed to the vapor being coated with a thin film of the material vaporized [135]. Usually the source material is placed inside a metal boat which is resistively heated using a large electrical current.

Electron beam evaporation process (shown in Figure 4.2(b)) is similar except an intense electron beam is adopted to heat the source material and causes the thermal evaporation. Materials with high melting point such as platinum and low thermal conductivity
such as SiO\textsubscript{2} can be vaporized with this method. Typically the evaporation rate is between 1 ~ 5Å/sec and can be controlled by adjusting the electron beam energy. Shadow masks [135] can be placed on the way between the source and the substrate, resulting in deposits only in pre-defined areas. The drawback of this evaporation method is the high temperatures involved, which is detrimental to the samples containing organic components.

![Schematic drawings of (a) Thermal evaporation and (b) E-beam evaporation.](image)

Figure 4.2. Schematic drawings of (a) Thermal evaporation and (b) E-beam evaporation.

### 4.1.3 Magnetron Sputtering

Magnetron sputtering [136] is another PVD process, in which atoms or molecules are removed from the surface of a target (Co, Ta, Si etc.) by bombarding it with ions from the plasma magnetically confined to this surface. The flux of material from the target
surface condenses onto the substrate surface and creates a uniform coating, as shown in Figure 4.3.

The biggest difference between sputtering and evaporation is that the atomic velocities are much more randomly oriented as they approach the sample surface, and this is why shadow effects seen in evaporation are rarely seen with sputtering. This difference arises mainly from the size of sputtering target and the sample-source. These two factors determine the amount of collimation of the flux. In electron beam evaporation flux collimation is achieved by using a small source placed far from the sample, while sputtering normally uses a large source which is more closely spaced to the sample, leading to an opposite effect.

Figure 4.3. Schematic diagram of magnetron sputtering system (taken from Ref. [137]).

Sputtering can deposit thin layers from a wide range of source materials because the source need not be heated to its melting point. The plasma can be generated by either a
large voltage (DC magnetron sputtering), or a high power radio frequency (13.5 MHz) signal (RF magnetron sputtering). The former is only well suited for depositing conducting materials because the plasma will not initiate under DC voltage if the target is insulating due to charge build up. However, by applying a high frequency AC voltage between the cathode and anode, the charge build up can be readily eliminated because the heavy Argon ions become immobile beyond a certain frequency (50 kHz) while light electrons can still easily follow the oscillatory voltage and neutralize the positive charge build up [138].

In the author’s Ph. D work, the silicon dioxide layer on the top of titanium oxide substrate is deposited by RF magnetron sputtering a Si target in the atmosphere of a mixture with oxygen and Argon gas. The details will be discussed in the next Chapter.
4.2 Lithography (Optical and Electron-Beam)

Lithography has been an indispensable technique with tremendous value to engineers and researchers in many technical fields. It has allowed rapid miniaturization of integrated circuits (ICs), and created countless new opportunities for studying and understanding the physics of the microscopic world [139]. In the author’s Ph. D work, both optical and electron-beam lithography have been used to fabricate CrO$_2$ nanostructures with lateral sizes ranging from a few microns, all the way down to 50 nanometers [26].

The basic process of photolithography is illustrated in Figure 4.5. Usually, the wafer surface is first coated with a thin layer of photosensitive material called photoresist (such as AZ5214-IR from Clariant [140]), then baked for certain amount of time and exposed to UV light through an optical mask [139,141]. During the exposure process, the resist which is exposed undergoes a chemical reaction and changes its chemical properties. The part exposed to light (in positive photoresist) or the part covered by the mask (in negative photoresist) is subsequently dissolved in the developer liquid (AZ327 developer). As a result, the images on the mask are precisely printed onto the photoresist, and the pattern then can be physically transferred to the thin film sample by either an etching back of the deposited material or a lift-off process after thin film deposition.

The resolution of optical lithography is limited by the wavelength of the UV light (~ 1 micron), thus making it improper to make submicrometric structures. However, electron beam lithography, which uses high energy electron beam instead of optical light for the exposure, can create much finer patterns (~ 10 nm) due to the small spot size of the electron beam. Furthermore, no physical mask is required during the e-beam lithography,
the electron beam is deflected and directly scanned over the e-beam resist coated sample by a computer controlled pattern generator (software NPGS [142]). In our lab, positive resist polymethyl methacrylate (PMMA) from MicroChem [143], is used for e-beam writing and sub-50 nm-sized nanostructures can be achieved.

Figure 4.5. Schematic of the processes used in photolithography (taken from Ref. [137])
4.3 Etching

Etching is the basic method of removing material from a surface. Usually, it is necessary to remove material only in certain areas. The areas that are not to be etched are protected by an etching mask. In many cases, however, the etch mask material will be removed at the same time. One measure of the quality of an etch process is the selectivity ratio, which is the relative etch rate of the mask layer to the layer being etched.

4.3.1 Wet Etching

This etching method utilizes liquid chemicals or reactive solution (etchant) to remove materials from the wafer or substrate, either by chemical reaction or by dissolution. The reaction products must be soluble and are carried away by the etchant solution. Different specialized etchants can be used to achieve different goals. For instance, buffered hydrofluoric acid (BHF) is widely used to etch silicon dioxide over a silicon wafer; piranha solution (H₂SO₄ 98% and H₂O₂ 30% in 3:1 ratio) are normally used in removing organic contaminants. In our work, chromium etchant type 1020 from TRANSENE company, INC. [144] is selected to remove the CrO₂ layer deposited on the TiO₂ substrate.

For most of the time, wet etching is highly isotropic except in crystalline materials. Usually, wet etching process is inexpensive and yields a high etching rate, a high selectivity and a high throughput. However, due to the properties of liquid, this method is improper for etching samples with feature size smaller than 3 μm, and it has been replaced by plasma etch in current industries.
3.3.2 Reactive Ion Etching (RIE)

Reactive ion etching (RIE) is an etching technology widely used in microfabrication process. It uses chemically reactive plasma to remove material deposited on wafers. The plasma is generated under low pressure (vacuum) by an electromagnetic field. High-energy ions from the plasma attack the wafer surface and react with it.

As shown in Figure 4.6, plasma is initiated in the system by applying a strong RF (radio frequency) electromagnetic field to the wafer platter. The field is typically set to a frequency of 13.56 megahertz, applied at a few hundred watts. The oscillating electric field ionizes the gas molecules by stripping them off electrons, thus creates the plasma. In each cycle of the field, the electrons are electrically accelerated up and down in the chamber, sometimes striking both the upper wall of the chamber and the wafer platter. At the same time, the much more massive ions move relatively little in response to the RF electric field. When electrons are absorbed into the chamber walls they are simply fed out to ground and do not alter the electronic state of the system. However, electrons absorbed into the wafer platter cause the platter to build up charge due to its DC isolation. This charge build up develops a large negative voltage on the platter, typically around a few hundred volts. The plasma itself develops a slightly positive charge due to the higher concentration of positive ions compared to free electrons.

Because of the large voltage difference, positive ions tend to drift toward the wafer platter, where they collide with the samples to be etched. The ions react chemically with the materials on the surface of the samples, but can also knock off (sputter) some material by transferring some of their kinetic energy. Due to the large amount of heat generated by the ion bombardment, the temperature on the surface of the wafer increases very fast,
which may cause photoresist reticulation and an uncontrollable etching speed and selectivity. As a result, if the etching process is long and needs to be controlled precisely, cooling of wafer is a must, which is usually achieved by the Helium backside cooling.

Due to the mostly vertical delivery of reactive ions, reactive ion etching can produce very anisotropic etch profiles, which contrast with the typically isotropic profiles of wet chemical etching [145].

![Figure 4.6. Schematic drawing of a reactive ion etching system.](image)

### 4.3.3 Ion Beam Etching (IBE)

Ion beam etching is a commonly used physical dry etching process with high directional anisotropy and low material selectivity. It uses an energetic, beam-collimated and highly directional ion source to collide with a substrate and physically mill material from the surface. This process starts with introducing Argon gas into a discharge chamber, then
an electrical current is applied to cathode, heating it and generating electrons via ther-
mionic emission. A discharge voltage is applied to accelerate the electrons to excite the
plasma. To increase the ionization rate, a magnetic field is usually employed to trap elec-
trons within the discharge chamber. Ions are directed toward the substrate through a ne-
gatively biased accelerator which attracts the positively charged ions. During the ion mil-
ling process, the plasma neutralizer adds electrons to the ion beam, it helps reducing the
charge build up on the target. The etching rate of ion milling depends on the beam energy,
density and the incident angle. Similar to the RIE process, wafer cooling is a must.

<table>
<thead>
<tr>
<th>Type of Etch</th>
<th>Wet Etching</th>
<th>Reactive Ion Etching</th>
<th>Ion Beam Etching</th>
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<td>Low</td>
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<tr>
<td>Selectivity</td>
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<td>Very poor</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

Table 4.1. Comparison of three types of etching processes.
4.4 Structural characterization

4.4.1 X-Ray Diffraction (XRD)

X-Ray diffraction (XRD) is a widely known structural characterization technique that can provide a broad range of information about the structure of materials, including the crystal phases and textures, film thickness, grain size and stress of unknown samples [146]. X-ray is generated by high energy electron bombardment on an element. Hot electrons are emitted from a cathode, and accelerated in a high field towards the target anode. The ionization of the target anode atom leaves a vacancy in the deep K shell, and electrons from outer shell fall down and emit the excess energy as an X-ray photon. Figure 4.7 shows the illustration of the basic XRD principle. When a monochromatic X-ray beam with wavelength $\lambda$ is incident onto a crystalline material at an angle $\theta$, diffraction occurs only when the distance ($d$) traveled by the rays reflected from successive planes differs by an integer number of wavelengths. This relation is better known as Bragg’s Law: $2d \sin \theta = n\lambda$. By varying the incident angle $\theta$ over a wide range of values, all of the various unit cell dimensions of the constituent materials in a polycrystalline sample can be measured.

Figure 4.7. An illustration of the basic XRD principle.
4.4.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is generally used to examine the surface of films and lithographically patterned structures. In a typical SEM, the specimen is scanned with an electron beam focused using magnetic fields. The electrons are either thermionically emitted from a tungsten cathode or emitted via field emission (FE) and then accelerated towards an anode. When incident electrons strike the sample, they will undergo multiple collisions as they penetrate the sample surface. This interaction leads to subsequent emission of electrons (secondary electrons) from the surface of the sample, with the number of electrons depending on the material and structure being scanned. These electrons are then detected to get a close replication of the surface topography. Figure 4.8 shows a schematic drawing of a typical SEM system.

Figure 4.8. Schematic drawing of the SEM imaging set-up (modified based on Ref. [147]).
SEM imaging usually requires little sample preparation for conducting samples. For insulating specimen, such as the (100)-TiO$_2$ substrate, a thin layer of conducting film such as gold or aluminum must be deposited onto the sample prior to imaging, in order to avoid the surface charging (see details in Chapter 5). The spatial resolution of the SEM depends on the electron spot size and the interaction volume, which is typically 10 - 50 nm.

### 4.4.3 Atomic and Magnetic Force Microscopy (AFM/MFM)

Atomic force microscopy (AFM) is one of the many scanned-proximity probe microscopes [148,149]. It operates by scanning a sample surface with a sharp tip, with end size as small as 10 nm. During operation, the tip is either directly in contact with (contact mode) or is quickly tapping on (tapping mode) the sample surface. The small changes in the tip height are monitored by an optical system measuring the laser beam reflected from the back of the cantilever, on which the tip is located. By scanning across the sample surface with the tip, one can image the morphology of a surface with up to 10 nm resolution. An illustration of the AFM is shown in Figure 4.9(a).

Depending on the nature of the tip and sample, AFM can measure a number of different forces, and thus how magnetic force microscopy (MFM) appears. Unlike typical AFM, a magnetically coated tip is first magnetized and then used to study magnetic materials. Thus, the tip-sample magnetic interactions are detected, which allows imaging of the magnetic fields just above the surface of the sample and reveals the domain structure of a patterned magnetic sample with nanometer resolution, as shown in Figure 4.9(b).
4.5 Vibrating sample magnetometer (VSM)

The vibrating sample magnetometer (VSM) is mainly used for measuring the hysteresis curve of bulk magnetic materials. It uses a set of coils to detect the AC magnetic fields generated by a sample in mechanical vibration with certain frequency. When placed in a magnetic field, ferromagnets can generate a dipole magnetic moment. As the ferromagnet vibrates periodically in the applied field, a periodical electrical signal (measured using lock-in amplifier) can be induced and detected by the coils, shown indicated in
The induced signal has the same frequency as the sample vibration and its amplitude will be proportional to the sample’s magnetic moment, size and relative position with respect to the coils. The absolute value of magnetic moment can be calculated by comparison with a standard Ni reference sample.

Since the sample can be rotated with respect the field and the detector, the VSM outstands itself with sophisticated angular capabilities. The resolution of a typical VSM is in the order of $10^{-5}$ emu. A lakeshore 7300 VSM [151] was used to measure the magnetic properties of CrO$_2$ thin films in this work.
4.6 Electrical transport measurement system

4.6.1 Liquid nitrogen (LN2) cryostat

A LN2 cryostat (Oxford Instruments [152]) in our lab is the standard system to do electrical transport measurement with temperature varying from 77 K to 350 K. The sample holder has an attached 25w cartridge heater on the back, which is mounted on the tip of a stainless steel rod and immersed in the environment of liquid nitrogen. 20 pin connectors around the sample holder allow us to measure multiple objects at the same time. A Lakeshore [151] 340 Temperature controller is used to precisely control the temperature with variance below 0.1 K.

In order to measure the magnetotransport properties also, two pairs of crossed electromagnets have been installed around the sample stage to provide a horizontal magnetic field in both the X and Y direction. The magnet currents are supplied by two Kepco [153] BOP36-12 power supplies, capable of producing fields up to 2500 Oe in each direction. The entire system is automated using Labview software [154].

4.6.2 Cryogen–free closed-cycle refrigerator (CCR)

CCR is a relatively new system that provides a convenient means of cooling samples to temperatures below 10 K, and can be used to perform a wide variety of optical and electrical experiments between ~ 8 K and 325 K (Janis Model CCS-350T [155]). CCR systems require no liquid helium or liquid nitrogen as a source of cooling. Instead, a closed loop of helium as is compressed and expanded, based on the Gifford-McMahon (G-M)
thermodynamic cycle. During the expansion phase of each cycle, heat is removed from the cold finger, on which the sample is mounted. A CTI Model 8200 compressor [156] is used to provide the high pressure helium gas needed for the cycle, and a heater and thermometer are installed on the cold finger and are used to precisely control the sample temperature.

Figure 4.11. A photograph of the closed-cycle refrigerator system in our lab, which is capable of cooling down to ~ 8 K without the need of liquid helium as a source of cooling.
Chapter 5

Fabrication of CrO₂ Nanostructures and Morphological Characterization

The detailed fabrication process of both polycrystalline and epitaxial chromium dioxide nanostructures is introduced and discussed in this Chapter. The key point of this process is the use of selective-area growth technique, which prevents the damage caused by various post deposition etching and allows us to study the nanocrystal growth process. We find that multiple grains are formed in the polycrystalline CrO₂ structures with size larger than 100 nm, however, below which only a single grain is allowed to exist due to the geometrical confinement. The lateral growth rate of epitaxial CrO₂ nanocrystals is found to be highly anisotropic, which is affected by both the orientation and the deposited thickness.
5.1 Fabrication of chromium dioxide (CrO₂) nanostructures

The fabrication of chromium dioxide structures at the nanometer scale is a challenging task. So far, there has been no single reliable recipe available. This is due to the metastable nature of this material because CrO₂ is not a thermodynamically stable phase at atmospheric pressure and room temperature, and it inevitably decomposes and forms a native oxide Cr₂O₃ layer on the surface. Prior to the author’s work, various methods have been attempted to pattern CrO₂ small structures such as reactive ion etching (RIE) [157], wet etching, argon-ion milling, and focused ion beam milling [158]. In all these methods, CrO₂ thin films are deposited and then etched to make small patterns, which increased the transformation from CrO₂ to Cr₂O₃, inevitably resulting in degradation of the quality.

In this work, we applied an alternative approach, i.e. the selective-area growth technique (SAG) [80], to make chromium dioxide structures. It utilizes the fact that during the chemical vapor deposition process, CrO₂ grows readily on the surface of TiO₂ but not on amorphous SiO₂ because CrO₂ has zero sticking coefficient on SiO₂ substrates [26]. This way avoids the post-deposition etching and subsequent reduction of CrO₂. Furthermore, we have extended the selective-area growth technique to enable the fabrication of high quality CrO₂ nanostructures with individual feature size smaller than 80 nm.

The experimental process is shown briefly in Figure 5.1. First, a layer of silicon dioxide (~ 100 nm) was deposited onto the TiO₂ substrate and then a 350 nm thick polymethylmethacrylate (PMMA) was spin coated onto the SiO₂ film. After baking at 185 °C for 30 min, a thin layer of chromium (Cr) was deposited by electron beam evaporation and patterns were then defined by e-beam lithography in a LEO 20 kV scanning electron mi-
croscope (SEM). After removal of the chromium layer in a Cr etchant solution, the developed PMMA was used as the etching mask for the reactive ion etching of the underlying SiO₂ layer, which is carried out in a CHF₃ atmosphere. The introduction of CHF₃ allows anisotropic etching for perpendicular sidewalls and high aspect ratio features. After the RIE of SiO₂, the remaining PMMA was removed using acetone and the sample was carefully cleaned in isopropanol (IPA) and de-ionized water before the CrO₂ deposition. Chromium dioxide was grown by metal organic chemical vapor deposition (MOCVD) using solid CrO₃ as the precursor. The deposition time is controlled strictly so as to achieve an intended thickness. Both polycrystalline and epitaxial CrO₂ nanostructures with sub-100-nm size can be readily obtained with this method. In the following subsections, we will explain these steps in greater detail.

1. Electron Beam Lithography

2. PMMA Development

3. RIE of SiO₂

4. Growth of CrO₂

Figure 5.1. Schematic diagrams of the process used to fabricate chromium dioxide nanostructures. Selective area growth technique plays an essential role here (Ref. [26]).
5.1.1 Rutile phase titanium dioxide (TiO$_2$) substrate preparation

There are mainly two types of titanium oxide existing in nature: anatase phase and rutile phase. Due to the lattice constant mismatch, only rutile phase TiO$_2$ can support the growth of CrO$_2$. In order to study the properties of CrO$_2$ nanostructure under different crystalline conditions, both single crystal and polycrystalline TiO$_2$ substrates have been used in this work.

Epitaxial (100)-TiO$_2$ substrates were purchased from CrysTec Company [159], which is transparent with size of 5 mm by 5 mm a piece. Finer-grain polycrystalline TiO$_2$ was home grown using the following steps:

i). Oxidize the silicon wafer in a high temperature (T = 1000 °C) oxidation furnace within oxygen rich atmosphere to form a 1 micron thick SiO$_2$ layer.

ii). Deposit a layer of titanium (~ 200 nm) using e-beam evaporation.

iii). Oxidize the Ti/SiO$_2$ substrate in a high temperature furnace (T = 750 °C) with oxygen applied for 2 hours. The silver-like Ti layer then becomes the transparent rutile phase TiO$_2$ layer.

iv). Cut the wafer (TiO$_2$/SiO$_2$) into small pieces and store in a jar with desiccant.

The TiO$_2$ substrate should be cleaned carefully before moving on to the next step. Usually, an ultrasonic cleaning in the sequence of acetone (2 min), isopropanol (2 min) and de-ionized water (5 min) is adopted in this work. Furthermore, diluted hydrogen fluoride solution may be applied to the epitaxial TiO$_2$ substrates to increase the strain effect [160].
5.1.2 Silicon dioxide (SiO₂) deposition

Load the sample (TiO₂ substrate) into the magnetron sputtering chamber and wait until the base vacuum reaches a pressure better than 1 x 10⁻⁷ Torr. Deposition is done via RF sputtering in a mixed argon-oxygen environment with the pressure 8.5 mtorr and an Ar/O₂ ratio of 3:1. A transmitted RF power of 150W is used throughout the deposition, and the deposition rate is controlled to be 1 Å per second or so.

The final deposition thickness of SiO₂ is about 100 nm, and the SiO₂ layer made in this way has been found to be free of any pinholes and have excellent insulating property. These two properties are of essential importance because pinholes can result in the deposition of CrO₂ at unexpected areas and the unwanted conductivity of the SiO₂ layer will cause complications in the subsequent transport measurement of CrO₂ nanostructures.

5.1.3 Electron-beam resist coating

A layer of e-beam resist (PMMA C4 from MicroChem [143]) is spin-coated onto the SiO₂/TiO₂ sample using a photoresist spinner with the final speed set to 5000rpm and the operation time set to 45 sec, which results in a thickness of ~ 350 nm for PMMA C4. Then, the sample is baked on a pre-heated oven (T = 185 °C) for 30 minutes.

5.1.4 Chromium deposition for charge dissipation

During electron beam lithography, accumulation of charge from the beam on the sample must be prevented because substrate charging may generate distortion overlay errors [161,162] and resist charging may prevent SEM inspection and e-beam writing down to sub-100 nm scale. For metallic or semi conductive substrate, this is accomplished by
grounding the substrate to the wafer holder with clips, which may have points that pierce through the resist layer to the substrate. For insulating substrates such as quartz or titanium dioxide, a thin layer of metal (gold, aluminum or chromium) can be placed on the sample after application of the resist layer to provide a conducting layer. Since the layer is thin, the high-energy electrons pass through the layer with little scattering and after exposure, the metal layer is removed with the appropriate etchant before the development of the resist. Another method to provide charge dissipation is to coat a layer of conducting polymer under or over the resist [163].

For the insulating SiO₂/TiO₂ substrate in this work, a thin layer of chromium (~5 nm) serves as the charge dissipation, which is deposited using DC magnetron sputtering a chromium target in pure argon atmosphere with pressure controlled around 1 mtorr.

5.1.5 Electron beam lithography

This is the most important step in the fabrication process. The quality of the writing directly results in the geometrical size of the final structures. A LEO1530 field emission SEM equipped with e-beam lithography system was used throughout this work, and the detailed process is listed as follows:

i). Load the sample into SEM chamber and pump down.

ii). Set the parameter HEIGHT Z to be 23 mm (FOCUS on the sample is around 3.8 mm) and Acceleration Voltage to be 20 kV.

iii). Set the Aperture Size to be 10 μm or 15 μm. This number affects the beam writing current (27 pA at 10 μm and 54 pA at 15 μm). Usually a smaller current is preferred when writing a pattern with sub-100 nm size.
iv). Adjust Rotate/Tilt, Aperture Alignment, Stigmation and Focus to achieve an optimal SEM image down to 10 nm scale.

v). Open Beam Blanker, toggle switch to NPGS, run Rencom32 program and open COM1 port. Set the system into NPGS Mode to check connection, and then go back to SEM Mode.

vi). At NPGS main window, click [Commands] → [Direct stage control] to get new focus data at several different places on the sample (usually close to corners). The NPGS program uses a linear relation (FOCUS = Ax + By + C) to fit the four points, and yield the FOCUS value at the center of the sample. The resulting RMS error should be no larger than 0.002.

vii). Set the system into NPGS mode and move the X-Y coordinate to the center of the sample (average value of the coordinates of the corners).

viii). Run pre-edited RF6 file and wait until e-beam writing is finished.

ix). Set the X-Y coordinate 20 mm away from the center of the sample and close the Rencom32 port. Set toggle back to SEM mode and Turn off beam blanker. Finally, turn off the acceleration voltage and vent SEM chamber.

5.1.6 Chromium removal and PMMA development

First, dip the e-beam-written sample in chromium etchant solution (from Transene Inc. [144]) for 30 seconds, and clean with de-ionized water. Then, the sample was developed in a 3:1 isopropanol (IPA) : methyl-iso-butyl-ketone (MIBK) mixture for 60 seconds, followed by rinsing in pure IPA and DI water. Finally blow the sample dried with N2 gas.
5.1.7 Reactive ion etching with CHF$_3$

One of the problems encountered in microfabrication process is the effective transfer of small features into semiconductor films or substrates. In reactive ion etching, this is especially problematic when the masking resist (such as PMMA) is particularly weak toward withstanding dry etching, or the feature size (~50 nm) is smaller than the thickness of the film (~100 nm) into which we desire to transfer the pattern.

For effective pattern transfer to the underlying SiO$_2$ layer using PMMA as a masking material in RIE, it was suggested that the PMMA etch rate can be highly reduced by using CHF$_3$ as a reactive gas in a low base pressure (~10 µTorr) [164]. The chemical reaction involved in the CHF$_3$ plasma during RIE produces less free fluorine concentration due to the formation of the radical HF in the gas phase, which is not easily dissociated. This reduction in the free fluorine concentration will decrease the formation of volatile compounds such as CF$_x$ on the PMMA surface, thus reducing the overall PMMA etch rate. Another advantage of the CHF$_3$ plasma is that it reacts with PMMA and produces a fluoropolymer. The fluoropolymer on the top surface of PMMA can be removed by new CHF$_3$ ion bombard, while those generated on the sidewalls can block the further reaction between CHF$_3$ and PMMA, resulting in a nearly vertical etching sidewall, i.e. high etching directionality. Finally, low base pressure reduces the oxygen concentration in the chamber, which also decreases the etching rate for PMMA layer.

During the RIE process, the surface temperature of the sample increases very fast due to the ion bombardment. Higher temperature increases the etching rate for PMMA but not for the underlying SiO$_2$ layer, resulting in a smaller etching selectivity. In order to solve this problem, cooling cycles are introduced in the etching process to keep the sample cool.
In our work, the SiO$_2$ RIE was carried out in a CHF$_3$ and Ar atmosphere at 15 mTorr. The gas flow was maintained as 25 sccm for each gas, which allows a good balance of physical sputtering and chemical etching processes. The plasma was generated at the RF power of 150W, resulting in around 295V self-bias voltage. The etching process lasts 1 minute per cycle and is shut off and cools for 2 minutes before next ignition. Five cycles are used to etch 100 nm thick SiO$_2$ layer. The SiO$_2$ etch rate in a 20 $\mu$m by 20 $\mu$m mesa is determined to be nearly 25 nm/min, with a selectivity of about 1:1 to PMMA for our RIE system. As the etch rate is lower in the reduced pattern size due to the micro-loading effect [165], the SiO$_2$ is over-etched a little to ensure a reliable pattern transfer and expose the underlying TiO$_2$ layer.

After RIE, soak the sample in acetone for 5 minutes to remove the PMMA residue, and then clean the fluoropolymer residue with piranha solution.

Figure 5.2. SEM images of a hexagonal lattice with the period of 400 nm. (a) Patterns in PMMA after e-beam lithography, and (b) patterns in SiO$_2$ after reactive ion etching using CHF$_3$ and removal of PMMA mask (30° tilted view).
5.1.8 Electrical contact pads defined by optical lithography

Electron beam lithography are usually adopted to write small features such as nanodots or nanowires due to its slow writing speed, big patterns like electrical contact pads are often defined by optical lithography.

The photoresist used in this work is AZ5214-IR from Clariant Inc. [140]. The biggest advantage of this photoresist is that both positive and negative exposure can be applied. The respective parameters are listed in the following:

**Positive Exposure:**

i).  Spin Coating AZ5214 (5000 rpm, 5000 rpm/s, 45 sec)

ii).  Bake on an oven pre-heated to 110 °C for 2 minutes.

iii).  Expose 20 seconds using UV-light with wavelength ~ 365 nm.

iv).  Develop in AZ327 developer for 1 minute and rinse in DI water.

**Negative Exposure:**

i).  Spin Coating AZ5214 (5000 rpm, 5000 rpm/s, 45 sec)

ii).  Softbake on an oven pre-heated to 95 °C for 1 minute and 45 seconds.

iii).  Expose 4 seconds using UV-light with wavelength ~ 365 nm.

iv).  Post exposure bake on an oven pre-heated to 125 °C for 1 minute.

v).  Fluid expose 0.7 minute (without mask).

v).  Develop in AZ327 developer for 1 minute and rinse in DI water.
5.1.9 Second reactive ion etching using CHF₃

With the parameter set to be the same as the first CHF₃ etching, the total etching time is controlled to be 4 minutes. No cooling cycle is needed in this step, since AZ4214 layer (~1.5 micron) is much thicker than the SiO₂ layer (~100 nm). After RIE, soak the sample in acetone to remove photoresist residue, then clean with IPA and DI water.

5.1.10 Chromium dioxide deposition using CVD

The CVD deposition reactor consists of a quartz tube placed inside a two-zone furnace, as shown in Figure 4.1. Chromium trioxide (CrO₃) powder, from Alfa Aesar [166], is used as the precursor and is loaded into a quartz boat in the source zone (preheated to 260 °C), whereas the substrates are placed on a tilted susceptor in the reaction zone (preheated to 395 °C). Prior to placement in the reactor, the substrates are ultrasonically cleaned in organic solvents (acetone and IPA), and are subsequently rinsed in distilled water and blown dry with N₂ gas. Oxygen is used as a carrier gas for the sublimed CrO₃ to be transported to the reaction zone, where it decomposes on the TiO₂ substrate to form CrO₂ with evolution of O₂. The phase purity and morphology of the films is dependent on the substrate, the source temperature, and the oxygen flow rate. We have obtained single-phase films at substrate temperatures of 390 – 400 °C, with a source temperature of around 260 °C and oxygen flow rate of 150 sccm.

In the beginning of deposition, a cleaned TiO₂ substrate is placed onto the susceptor, open the tube from the right side, and then slide the susceptor to the center of the right oven. Close the tube, wait 10 minutes for stabilizing the temperature (395 °C). Then open the left side of the tube, slide the quartz cup with 30 mg CrO₃ precursor into the first
oven (preheated to 260 °C), and close the tube. CrO$_2$ deposition starts after 8 minutes (until all the power-like CrO$_3$ becomes a sintered solid) with the deposition rate determined to be roughly 1000 Å in 17 minutes. After deposition, first turn off the left oven and open its cap to air, wait 10 minutes, and then open the tube to pull out the precursor. (Danger: do not pull out the precursor while it is hot, CrO$_3$ is cancer risk [166]). Turn off the right oven and open it to air, give the TiO$_2$ substrate 30 minutes to cool down to room temperature before taking it out. Some orange powders always condense on the right side of the tube, just right out of the oven, which are non-consumed CrO$_3$ and can be easily rinsed off with DI water. Also, clean the tube with chromium etchant [144] after each deposition for the next use.

We have found that the deposition of CrO$_2$ is highly sensitive to the surface of the substrate, and thus the substrate cleaning procedure is critical and key for the deposition. Furthermore, CrO$_2$ grows readily on a clean TiO$_2$ surface, it does not deposit on amorphous SiO$_2$ (growth inhibition mask). Therefore, the spatial growth of CrO$_2$ is controlled selectively by appropriately prepatterning the substrate surface, i.e., CrO$_2$ deposition can only happen at the windows opened on the SiO$_2$ layer (TiO$_2$ exposed).

Our method utilizes electron beam lithography coupled with selective area epitaxy MOVCD to explicitly define the physical parameters of CrO$_2$ nanostructures, as well as the growth location, on an individual basis. This technique is advantageous as it leaves the crystal surface unaffected and promotes the growth of coherent, dislocation free structures, also it can form the basis for more advanced components in which devices with different functionality are integrated on the same chip.
5.2 Morphological characterization of CrO₂ nanostructures

The crystallographic properties of the deposited CrO₂ structures are solely dependent on the TiO₂ substrate. A polycrystalline TiO₂ substrate can support the growth of polycrystalline CrO₂, while a single crystal TiO₂ substrate gives epitaxial CrO₂ structures [80]. There are two types of CrO₂ nanostructures discussed in the following, respectively.

5.2.1 Polycrystalline CrO₂ nanostructures

The scanning electron microscopy (SEM) images of polycrystalline CrO₂ nanodot arrays are shown in Figure 5.3(a) and 5.3(b). We can see that multiple grains are formed in the dots with diameter \( d = 250 \) nm. However, when \( d \) is reduced to about 100 nm, each dot contains only one single grain. This can be understood by considering that, when the size of the holes on the SiO₂ template is smaller than the mean grain diameter of the TiO₂ substrate (~ 100 nm), there is only one TiO₂ grain below each SiO₂ hole to support the growth of CrO₂. Upon increasing the thickness, the deposited CrO₂ reaches the top of the mask and then overgrows both vertically and laterally. Figure 5.3(c) displays the overgrown CrO₂ from 150 nm sized holes. As can be seen, the borders of the holes are completely covered by the CrO₂ above the SiO₂ mask. Figure 5.3(d) displays the SEM image of a 200 nm wide overgrown multi-grain ring structure. Figure 5.3(e) and 5.3(f) show the single-grain rings and single-grain nanowire structures, which are due to its narrow width. Furthermore, a 150 nm wide zigzag wire and a sub-100 nm wide nanowire with electrical pad attached to the left are shown in Figure 5.3(g) and 5.3(h). The clear grain facets and borders reflect that every grain was grown naturally without any postdeposition damage [167].
Figure 5.3. SEM images of polycrystalline CrO$_2$ nanostructures: (a) 100 nm sized dots array, (b) 250 nm sized dots array, (c) overgrown CrO$_2$ from 150 nm sized holes, (d) a multi-grain ring structure, (e) single-grain ring structures, (f) a single grain nanowire, (g) a zigzag-shaped nanowire with 150 nm in width and (h) a sub-100 nm wide nanowire with electrical pads attached to the left (Ref. [167]).
5.2.2 Epitaxial CrO$_2$ nanostructures

Figure 5.4(a) displays the SEM image of 100 nm sized epitaxial chromium dioxide nanodots. As can be observed, all the dots are distinct and aligned in the same crystal direction. Figures 5.4(b) – 5.4(d) show the morphology of the CrO$_2$ nanodots with different deposited thicknesses $t$. All the dots grew naturally into a rectangular shape, which implies that the lateral (in-plane) growth rate was anisotropic during the CVD process. Otherwise, the dots would form a round shape instead of a rectangular one, since the anti-dot patterns predefined on the SiO$_2$ template were circular. Furthermore, we can see that the aspect ratio of the rectangle is not a constant, and changes with the CrO$_2$ thickness. Hence, the mean lateral growth rate $V$ is affected by both the direction, represented by angle $\theta$ in Figure 5.4(f), and the thickness $t$ of the deposited CrO$_2$.

The CrO$_2$ nanocrystal growth process can be physically described as follows. At the beginning of the deposition, CrO$_2$ first covered the TiO$_2$ at the bottom of the holes, but not the adjoining SiO$_2$ due to the selective area growth. Then beyond a certain thickness, the deposited CrO$_2$ deformed with a preferential lateral growth direction along the c axis, as evidenced in Figure 5.4(b). This means that when $t$ was small, $V(\theta, t)$ was maximum for $\theta_m \approx 0^\circ$. It can be attributed to the fact that there is a large lattice mismatch between TiO$_2$ and CrO$_2$, of -3.79% along the b axis ([010] direction) and only 1.48% along the c axis ([001] direction). The chemical vapor deposition favors the growth along the [001] direction for higher lattice match in order to reduce the internal strain energy. When $t$ increased, CrO$_2$ starts to overgrow laterally over the amorphous SiO$_2$ mask. We can see in Figure 5.4(c) that in the meanwhile a rectangular shape with long side parallel to the c axis was formed for every dot, indicating the maximum $V(\theta, t)$ was achieved at an angle $\theta_m$ between...
0° and 45°, more specifically, the diagonal direction of the rectangle. Upon further increasing the amount of overgrown CrO₂, the aspect ratio of the rectangular dots gradually became smaller and stabilized to 1. Our result reveals that when \( t \) is large ( ≥ 250 nm), \( V(\theta,t) \) is maximum for \( \theta_m = 45° \) ( [011] direction ) giving every dot a square shape. The preferred lateral growth along the [011] direction can also be observed in epitaxial CrO₂ zigzag nanowire shown in Figure 5.4(e).

Figure 5.4. SEM images of single crystal CrO₂ nanostructures grown on (100)-TiO₂ substrate: (a) 100 nm sized dot array, 250 nm sized dot array with different thicknesses (b) \( t = 100 \) nm, (c) \( t = 160 \) nm, and (d) \( t = 250 \) nm; (e) a 100 nm wide zigzag wire with overgrown CrO₂ along the [011] direction, and (f) schematic diagram for the mean lateral growth rate \( V \) dependent on the orientation, represented by angle \( \theta \).
At this point, the detailed kinetic process for the transformation from a high-aspect-ratio rectangle to a square is unknown. However, we believe that the anisotropic surface binding energy drives this CrO$_2$ nanocrystal growth. Other factors, such as the internal strain due to the lattice mismatch, may also play an important role.

Finally, as a comparison, the SEM image for several polycrystalline and epitaxial CrO$_2$ nanostructures are shown in Figure 5.5.
5.3 Summary

In this Chapter, we present a new method to fabricate both polycrystalline and single crystal chromium dioxide nanostructures. The use of the selective-area growth technique prevents the damage caused by postdeposition etching and allows us to study the nanocrystal growth process. Multiple grains were formed in the polycrystalline CrO$_2$ dots larger than 100 nm, however, below which only a single grain was allowed to exist. The lateral growth rate of epitaxial CrO$_2$ nanocrystals was found to be highly anisotropic, which is affected by both the orientation and the deposited thickness, and the epitaxial lateral overgrowth rate was found to be maximum at the [011] directions of (100)-TiO$_2$ substrate.
Chapter 6

Magnetic Domain Configurations of Epitaxial CrO$_2$ Nanostructures

Magnetic domain structures of submicrometric epitaxial CrO$_2$ fabricated using selective-area growth technique were studied by magnetic force microscopy. In-plane, lamellar domain structure with fragmented walls aligned along the magnetic easy axis direction is observed, indicating the existence of a large magnetocrystalline anisotropy. A classical model for ferromagnetic materials with a uniaxial anisotropy was used to explain this domain configuration. Estimates of the domain wall energy density and exchange stiffness constant for CrO$_2$ were obtained.
6.1 Introduction

Spintronics is an emerging area, where the electron spin (together with the charge) plays an active role in storing and transferring information [9]. In this area, half-metallic ferromagnets have been extensively investigated for realizing spin-dependent devices with high magnetoresistance. These materials have a band gap in the minority spin density of states near the Fermi level and therefore exhibit a 100% spin polarization. Among these materials, chromium dioxide (CrO$_2$) is one of the few experimentally proven half metals and possesses the largest spin polarization so far reported [11,6].

On the other hand, the study of magnetic nanostructures has also been a very active research field. One of the reasons for this is that applications in ultrahigh-density magnetic recording require the element dimensions to be reduced down to the nanometer scale. Also, interesting changes in the magnetic behavior of nanostructures are expected as the overall size approaches some critical length [20,1]. Hence, the study of the properties of nanosized half-metallic ferromagnets is a very promising field. In this Chapter, we fabricated epitaxial CrO$_2$ nanostructures and investigated both the remanent and field-dependent magnetic domain configuration of these elements using magnetic force microscopy.

6.2 Magnetic domain configurations of CrO$_2$ nanostructures

Chromium dioxide nanostructures with nanowire, ring and dot shapes have been fabricated on the same substrate to ensure identical magnetic and structural properties. The sample was first saturated along the easy axis ([001] direction) by applying a magnetic field of 2 kilogauss and then imaged in either the remanent or the field-dependent state using magnetic force microscopy (MFM). The MFM images were obtained with a Digital
Instruments nanoscope IIIa scanning probe microscope [168] in tapping mode with the scanning tip magnetized along the z direction (perpendicular to the sample surface).

### 6.2.1 Domain structures in remanent state

Figures 6.1 shows the MFM images of CrO$_2$ nanowires of various widths aligned along the [001] and [010] directions. In Figure 6.1(a), all the domains are aligned in plane along the magnetic easy axis. It is clear that the magnetic stray field signals at the element ends are very strong even for the 100 nm width, with no out-of-plane field observed in the

![Figure 6.1](image_url)

Figure 6.1. MFM images of submicron-sized CrO$_2$ wires with different widths aligned (a) along the [001] direction and (b) along the [010] direction. The thickness of the wires is around 100 nm. All the images were obtained at remanence after a saturation in a magnetic field applied along the easy axis direction. The schematic pictures shown nearby are the most probable domain configurations.
rest of the wire. This indicates a high quality single domain structure with a fully in-plane magnetization. For the wires in Figure 6.1(b), lamellar domain structures with fragmented walls, aligned mainly along the easy axis direction, are observed. Each wire is either magnetized parallel or antiparallel to the [001] direction, across its width, leading to an alternating contrast in the MFM image. A similar result has been reported recently for epitaxial CrO$_2$ wire with 2 µm width [169]. This domain configuration implies that a strong magnetocrystalline anisotropy exists in the [001] easy axis direction for these epitaxial chromium dioxide elements. The formation of multiple domains can be attributed to the competition between magnetostatic energy and domain wall energy, which will be discussed in detail later.

The magnetic image of an epitaxial CrO$_2$ ring in the remanent state is displayed in Figure 6.2(a). Unlike the vortex and onion states found in other ferromagnetic rings [123], the epitaxial CrO$_2$ ring displays a much more complicated domain structure. As can be seen, two large parallel domains are formed in the upper and lower parts of the ring and separated by many relatively small antiparallel domains in between. This configuration is consistent, again, with the existence of a strong uniaxial anisotropy along the easy axis direction, as found in Figure 6.1(b). The strong magnetocrystalline anisotropy is more obvious in the MFM image of the Y-shaped structure shown in Figure 6.2(b). The shape anisotropy induced in this structure is almost negligible in comparison to the uniaxial anisotropy, given that every domain is aligned along the magnetic easy axis.

Epitaxial CrO$_2$ nanodots with a diameter of 250 nm also show a single domain configuration along the [001] direction, as displayed in Figure 6.2(c). These dots exhibit a strong signal-to-noise ratio and a strong magnetocrystalline anisotropy which dominates
Figure 6.2. MFM images of submicron-sized CrO$_2$ structures with (a) a ring with 300 nm width, (b) a Y-shaped pattern with one arm aligned along the magnetic easy axis direction and (c) a portion of square lattice of 250 nm sized nanodots. The thickness is around 100 nm. All the images were obtained at remanence after a saturation in a magnetic field applied along the easy axis [001] direction. The schematic pictures shown nearby are the most probable domain configurations.

the shape anisotropy contribution, which suggest that epitaxial CrO$_2$ nanodots are a potential candidate for high-density state storage media [170].

We also found that the domain configurations for different wires aligned along the hard axis direction were closely related to the wire aspect ratio. As indicated in Figure 6.3(a), the domain width $d$ can be calculated approximately by dividing the length of the wire by the number of domains, while the domain length $L$ is roughly the width of the wire. The plot in Figure 6.3(b) shows that there is a linear relationship between the domain width and length. This result is consistent with the model for a uniaxial sheet of magnetic material with lamellar domain formation [36].
Figure 6.3. (a) Schematic drawing including the definitions of domain length $L$ and width $d$. (b) Domain width plotted vs. domain length for several typical CrO$_2$ lines aligned along the [010] axis. The width is calculated by dividing the length of the wire by the number of observed domains. The line is the best fit to the data according to theoretical predictions.

By minimizing the total energy density, including magnetostatic and domain wall energy, the equilibrium wall spacing for small thickness $t$ can be written as [36]:

$$d = L \frac{\sigma_d}{\sqrt{1.7 \mu_0 M_s^2 t}}$$

where $\sigma_d$ is the domain wall energy density, and $M_s$ is the saturation magnetization, which has a value of 475 emu/cm$^3$ for CrO$_2$ at room temperature. The domain wall energy density can be estimated to be 0.25 erg/cm$^2$ for a thickness $t = 100$ nm. On the other hand, for this
uniaxial case with an antiparallel domain configuration, the domain wall energy density can be approximated as:

$$\sigma_d \sim \sqrt{AK_u}$$

where $K_u$ is the uniaxial anisotropy constant, which gives a value of around $1.43 \times 10^5$ erg/cm$^3$ for an epitaxial CrO$_2$ thin film with $t = 100$ nm [17]. Thus, the exchange stiffness constant $A$ is estimated to be $4.37 \times 10^{-7}$ erg/cm, which is very close to the value of $4.6 \times 10^{-7}$ erg/cm calculated from the Curie temperature of chromium dioxide.

### 6.2.2 Field-dependent magnetic domain evolution

We also investigated the magnetic switching behavior of the epitaxial chromium dioxide nanowires using field dependent MFM. The sample was first saturated along the magnetic easy axis ([001] direction) and then imaged with a field $H$ applied in the same direction. Figure 6.4 displays the MFM images of CrO$_2$ wires of various linewidths $w$ aligned along the [010] axis under three different external fields.

A single domain structure with magnetization along the applied field direction was observed in Figure 6.4(a) for the epitaxial wire with $w = 1$ µm. Upon decreasing the linewidth, multi-domain structures were formed with a small number of domains having opposite polarities. This result can be explained by considering the demagnetizing field $H_d$, which was found to be roughly proportional to the inverse of linewidth $1/w$ [171]. When $w$ decreased from 1 µm to 200 nm, the internal field, $H_{int} = H_{250 \text{ Oe}} - H_d$, dropped significantly and thus was energetically unfavorable to maintain a single domain structure.
Figure 6.4. Magnetic field dependent MFM images of epitaxial CrO$_2$ nanowires aligned along the [010] direction with different linewidths. The field is applied in the [001] direction with value $H$: (a) 250 Oe (b) 100 Oe (c) 0 Oe (d) -100 Oe and (e) -250 Oe.
In Figure 6.4(b) where the external field $H$ was reduced to 100 Oe, the nucleation of antiparallel domains can be clearly observed as the number of domains with the magnetization reverse to the field direction increased.

When the magnetic field was further reduced to zero, the MFM image reflects the remanent magnetization state, which is displayed in Figure 6.4(c). A striplike domain structure, with magnetization parallel or antiparallel to the magnetic easy axis, was observed. It should be noted that the remanent state of the epitaxial CrO$_2$ nanowires are determined mainly by both the shape and magnetocrystalline anisotropy. The former favors an alignment of the magnetic moment parallel to the wire axis, while the latter prefers the magnetic easy axis direction. In our case, the wire axis is perpendicular to the magnetic easy axis, which means that these two effects are in competition with each other. The existence of striplike domain configuration even for the wire with $w = 200$ nm indicates that the magnetocrystalline anisotropy in epitaxial CrO$_2$ is very strong, which makes the shape induced effect almost negligible. Upon further increasing the field in the reverse direction, domains start to annihilate and a similar reversal process can be observed, as shown in Figure 6.3(d) and 6.3(c).

### 6.3 Summary

We have studied the domain configuration of several CrO$_2$ patterns grown epitaxially on (100)-TiO$_2$ including nanodots, nanowires, and ring structures using MFM. The in-plane, striplike, domain structures with domain walls aligned mainly along the [001] direction indicate a strong magnetocrystalline anisotropy, which makes the shape aniso-
entropy contribution almost negligible. We have also found that all the domains tend to have a similar aspect ratio. This can be understood with a classical model for uniaxial magnetic films. We have also investigated the magnetic reversal process of epitaxial CrO₂ nanowires. Our results show that the epitaxial CrO₂ nanostructures have the potential to be applicable in spintronic devices.
Chapter 7

Electronic Transport and Magnetoresistance in CrO₂ Nanowires

In this Chapter, we study and compare the electrical and magnetic behavior of sub-micron-sized polycrystalline and epitaxial CrO₂ wires, grown using a selective-area growth technique. Low-temperature transport measurements have shown that the dc resistivity of polycrystalline CrO₂ wires is strongly dependent on the linewidth. Below a critical temperature, a transition from a positive to a negative temperature coefficient of resistivity is observed. Magnetotransport measurements indicate that the MR behavior of polycrystalline CrO₂ wires is dominated by the shape anisotropy; however, for epitaxial wires, both the shape and magnetocrystalline anisotropy play important roles, and the resulting MR properties are found to be closely related to the orientation of the wire axis. By studying the MR curves, we inferred the internal magnetic domain structures in various single crystal CrO₂ wires and found that the spin-dependent transport is much stronger across a grain boundary than a magnetic domain wall.
7.1 Experimental procedure

Chromium dioxide films can be grown on a rutile-phased titanium dioxide (TiO$_2$) substrate by metal organic chemical vapor deposition (MOCVD) using solid CrO$_3$ as a precursor [160]. The crystal properties of CrO$_2$ made in this manner are primarily dependent on the substrate. In our experiments, epitaxial CrO$_2$ structures were deposited on (100)-oriented single crystal TiO$_2$ substrates, while the polycrystalline CrO$_2$ elements were deposited on polycrystalline TiO$_2$ film, which was obtained by oxidizing an electron beam evaporated titanium film at 800 °C for one hour (the titanium film was deposited on a SiO$_2$-covered silicon wafer).

To make CrO$_2$ nanowires we have adopted a method known as the selective-area growth technique. This method utilizes the fact that during the MOCVD process, CrO$_2$ grows readily on the surface of TiO$_2$ but not on amorphous SiO$_2$ [80]. The detailed fabrication process which we used has been discussed in previous Chapters [26].

Due to the instability of chromium dioxide (i.e., decompose into Cr$_2$O$_3$ on the surface), we use this material itself as the contact to measure the electrical properties of CrO$_2$ nanowires. Furthermore, in our case, the length of the wires is fixed at 100 micron and thickness is controlled to be around 100 nm. Most of the transport measurements were carried out over a temperature range from 77 K to 300 K in a liquid nitrogen cryostat. Two small electromagnets are used to provide a maximum magnetic field of 3 kOe in the plane of the sample. The rest of the measurements were done in a SQUID magnetometer equipped with a 4.8 Telsa superconducting magnet. The direct current (dc) resistance of samples was measured in a conventional four-probe configuration and the voltages were recorded by a Keithley multimeter [172].
7.2 Polycrystalline CrO$_2$ nanowires

Figure 7.1 displays scanning electron microscopy (SEM) images of two polycrystalline CrO$_2$ wires with linewidths of $w = 100$ nm and $1 \mu$m, respectively. It can be observed that the polycrystalline wires are composed of many small single crystal grains with different crystal directions, and neighboring grains are separated by very thin intergrain...

Figure 7.1. SEM images of two polycrystalline CrO$_2$ wires with linewidths (a) $w = 100$ nm and (b) $w = 1 \mu$m. The small structures seen above and below the CrO$_2$ wires are polycrystalline TiO$_2$ nanograins covered by amorphous SiO$_2$. 
regions (grain boundaries). Due to the additional lateral confinement from the SiO₂ sidewall, the average grain size decreases slightly with decreasing linewidth. Furthermore, because the nanowires were made using the selective-area growth technique, no postdeposition damage is introduced, as indicated by the clear crystal borders and grain facets shown in this figure.

To study the different contribution from electron scattering at grains and grain boundaries, we performed low temperature transport measurements on polycrystalline CrO₂ nanowires and the results are as follows.

### 7.2.1 Electrical properties of polycrystalline CrO₂ nanowires

The temperature dependence of the resistivity $\rho(T)$ in polycrystalline CrO₂ wires with different linewidths is shown in Figure 7.2. We can see that for the wire with the largest width $w = 5 \, \mu m$, the resistivity increases with increasing temperature, showing a positive temperature coefficient of resistivity (TCR), defined as $\alpha = (1/\rho)d\rho/dT$, over the full temperature range. However, for wires with smaller widths, there is a critical temperature $T_m$ corresponding to a resistivity minimum, below which the resistivity increases with decreasing temperature, exhibiting a negative TCR. In addition, the absolute magnitude of resistivity at all temperatures increases with decreasing linewidth. To confirm the observed results and to exclude possible effects due to other factors, e.g., the decomposition of CrO₂ into Cr₂O₃, the resistance-temperature curve was measured in both directions (i.e., during heating and cooling of the sample), and the two datasets coincide very well in all cases.
The SEM results indicate that the polycrystalline CrO$_2$ nanograins are separated by grain boundaries. Therefore, both the electron scattering within the grains and across these grain boundaries contribute to the overall resistance of the wire. However, the resistivity of single crystal bulk CrO$_2$ thin films is known to be very small, especially at low temperatures (only a few $\mu$Ω·cm at 77 K) [18]. Thus, the resistivity contribution from scattering at the interfaces between grains is likely to be increasingly important when temperature is lowered.
To explain quantitatively the grain boundary effect on the transport properties, we adopt a model proposed by Reiss [173]. A reduction in the grain size obviously leads to an increase in the density of grain boundaries, and when the grain size is comparable to the electron mean free path (MFP), every grain acts like a potential well, with the interfaces functioning as energy barriers. As a result, a certain fraction of conduction electrons are localized within the well, with the measured resistivity being dependent solely on those electrons which tunnel through all the boundaries along the MFP. This effectively results in a decrease in the effective number of the conduction electrons. Therefore, the total conductivity can be written as:

\[
\sigma = \left(\frac{ne^2l_\infty}{m_e\nu_F}\right)G(l_\infty, D, \Gamma) \quad \text{(7.1)}
\]

where \( ne^2l_\infty/m_e\nu_F \) is the conventional Drude formula with \( l_\infty \) being the bulk MFP which describes the scattering of the electrons inside the grain, \( D \) is the mean grain dimension, \( \Gamma < 1 \) is the mean transmission probability of an electron through a boundary, and the total transmission function \( G(l_\infty, D, \Gamma) \) reflects the influence of grain boundaries on the overall conductivity.

Based on some experimentally observed dependences, Reiss claimed that the reduction of the conductivity depends exponentially on the number of grain boundaries per MFP \( (l_\infty/D) \). In this case, the function \( G \) can be approximated by a power law [173]:

\[
G(l_\infty, D, \Gamma) \approx \Gamma^{l_\infty/D} \quad \text{(7.2)}
\]

Therefore, from Eq. (7.1) and (7.2), we can express the resistivity of a polycrystalline CrO\(_2\) thin film as:
\[ \rho_{\text{film}} = \rho_\infty(T)^{\frac{-l_\infty}{D}} \equiv \rho_\infty(T) \exp \left[ \frac{AC_0}{D\rho_\infty(T)} \right] \] .................(7.3)

where \( A = -\ln \Gamma \), \( C_0 = m_e v_f / ne^2 \), and \( \rho_\infty(T) = C_0/l_\infty \). The parameter \( C_0 \) is independent of temperature, and the function \( \rho_\infty(T) \) represents the resistivity contribution from electron scattering inside the grains.

Generally, when the linewidth \( w \) and thickness \( h \) of a metal film are reduced down to a very small scale, the electron scattering at the film surfaces (the top and bottom surface as well as the sidewalls of a wire) introduces an extra contribution \( \rho_{\text{surface}}(w, h) \) to the wire resistance, and this term is highly dependent on the ratio between the dimensions \((w, h)\) and the electron MFP [174,175]. However, the smallest wire in our measurements has dimensions of 100 nm, which is larger than the CrO\(_2\) electron MFP (around 30 nm at 77 K). Therefore, in our case, the contribution from the surface scattering is negligible and the resistivity of a polycrystalline CrO\(_2\) wire can be approximated from Equation (7.3):

\[ \rho_{\text{wire}}(w, T) \approx \rho_\infty(T) \exp \left[ \frac{A(w, T)C_0}{D(w)\rho_\infty(T)} \right] \] ............(7.4)

**Linewidth Dependence.** In polycrystalline CrO\(_2\) wires with large linewidths (a few microns or larger), each grain has several neighbors. When a current is applied, the conduction electrons take the path of least resistance by passing preferentially through the grain boundaries which have relatively high transmission probabilities. However, when the linewidth is reduced, the number of neighboring grains decreases significantly, and electrons are forced to travel along the wire axis in spite of the relative conductivity of the grain
boundaries. Therefore when reducing \( w \), the effective resistance of the grain boundaries will increase, leading to a smaller mean transmission probability \( I(w, T) \) and higher \( A(w, T) \) value. On the other hand, as shown in Figure 7.1, the mean grain diameter \( D(w) \) decreases when \( w \) is reduced. Taken together, these two effects result in the increase of \( \rho_{\text{wire}}(w, h) \) for smaller linewidths at any given temperature. This dependence is consistent with our experimental data.

(ii) Temperature Dependence. First, the mean transmission probability \( I(w, T) \) can be assumed to be weakly dependent on the temperature, i.e., \( A(w, T) \approx A(w) \), because it is most closely related to the structure of the grain boundaries. Additionally, the bulk resistivity \( \rho_\infty(T) \) of a metal typically has two contributions: One is the impurity scattering term \( \rho_0(T) \), which is temperature independent. The other term comes from temperature dependent inelastic scattering, which scales approximately as \( aT^\gamma \). Therefore, the bulk resistivity can be written as \( \rho_\infty(T) = \rho_\infty(T) + aT^\gamma \) [176]. The best fits to the data, based on Equation (4) and the above two assumptions, are shown in Figure 7.2 as solid lines. We can see that the agreement is good, indicating that the transport behavior of polycrystalline CrO\(_2\) wires is well-described by the grain boundary scattering model.

The values of the fitting parameters which are listed in Table 7.1 show that the bulk resistivity \( \rho_\infty(T) \) is much larger than the resistivity measured for epitaxial CrO\(_2\) bulk films [18], especially at low temperatures. This discrepancy can be partly attributed to the thickness dependent strain effects, which arise from the lattice mismatch between the TiO\(_2\) substrate and the CrO\(_2\) film [177]. The thickness of our CrO\(_2\) sample is around 100 nm; at this value, the strain induced by the lattice mismatch is not fully released. On the other hand, for polycrystalline CrO\(_2\) nanowires, the stress from the SiO\(_2\) sidewalls, which con-
fine the lateral growth of CrO₂, may also play a role. The combination of these effects introduces many lattice defects inside the CrO₂ nanograins and leads to a higher effective resistivity. Furthermore, during the curve fitting we assumed that $\rho_\infty(T)$ was identical for all the linewidths. However, upon reducing $w$, the resistivity from scattering inside the grains is likely to increase because the strain effects from the SiO₂ sidewalls increase. This probably explains that in Figure 7.2 the theoretical predictions start to deviate from the experimental results for the smallest wire width (100 nm).

<table>
<thead>
<tr>
<th>Linewidth $w$ (nm)</th>
<th>100</th>
<th>150</th>
<th>550</th>
<th>5000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AC_0/D$ (µΩ·cm)</td>
<td>317.4</td>
<td>291.5</td>
<td>236.1</td>
<td>177.2</td>
</tr>
<tr>
<td>$\rho_0$ (µΩ·cm)</td>
<td></td>
<td>140.08 ± 1.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ (µΩ·cm·K^{-γ})</td>
<td>0.0056 ± 0.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$γ$</td>
<td></td>
<td>1.98 ± 0.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1. Best-fit parameters, obtained from fits to the resistivity measurements of polycrystalline CrO₂ wires, as shown in Figure 7.2.

If we assume that the electron MFP of CrO₂ grains at zero temperature is not very different from the theoretical value predicted for large CrO₂ films, which is 70 nm [15], the constant $C_0$ can thus be estimated to be $C_0 = \rho_0(0)l_0(0) \approx 9.8 \times 10^{-4}$ µΩ·cm². Additionally, the mean grain size $D$ is about 100 nm, as shown in Figure 7.1. Hence, the mean transmission probability $Γ$ can be determined to be on the order of $10^{-1}$, indicating that neigh-
boring grains are coupled with each other. We can also estimate the resistivity $\rho_{\text{surface}}(w)$ due to surface scattering, an effect which was neglected during the curve fitting. The effects of element geometry on the resistivity of a metal thin film were discussed by Fuchs and Sondheimer, and their conclusion, summarized as the FS model, was that the surface resistivity can be approximated as $[174,175]$:

$$
\rho_{\text{surface}}(w) = \frac{3}{8}(1 - P)\rho_\infty(T)l_\infty(T)\left[\frac{1}{w} + \frac{1}{h}\right]
$$

where $P$ represents the fraction of electrons elastically reflected by the surfaces, and $h$ is the thickness of the sample (100 nm). If we assume, as a worst-case scenario, that $P$ is equal to zero, and $\rho_\infty(0)l_\infty(0) = C_0$, then $\rho_{\text{surface}}(w)$ is calculated to be 37 $\mu\Omega\cdot$cm for $w = 5$ $\mu$m and 74 $\mu\Omega\cdot$cm for $w = 100$ nm. These values are more than one order smaller than the total wire resistivity, showing that the decision to neglect the surface scattering contributions was reasonable and consistent with the experimental results.

Figure 7.3 displays the temperature dependence of the grain boundary resistivity and the grain resistivity $\rho_\infty(T)$ of polycrystalline CrO$_2$ wires with various widths. The direct contribution from the grain boundaries is determined by subtracting the grain resistivity from the resistivity of the whole wire:

$$
\rho_{\text{grain boundary}}(w,T) = \rho_{\text{wire}}(T) - \rho_\infty(T)
$$

It is clear that upon reducing the temperature, or the sample linewidth, the electron scattering probabilities at the grain boundaries increase greatly, as a result of an increased number of grains per electron MFP.
Figure 7.3. Temperature dependence of the gain boundary resistivity (open markers) and resistivity from scattering within the gains (solid line) for polycrystalline CrO\(_2\) wires with different linewidths.

The temperature coefficient of resistivity can be calculated by taking the derivative of the logarithm of Equation 7.4, where again \(I(w)\) is assumed to be temperature independent again:

\[
\text{TCR} = \frac{d \ln \rho_{\text{wire}}}{dT} = \frac{d \rho_{\infty}(T)}{\rho_{\infty}(T)dT} \left(1 - \frac{A(w)C_0}{D(w)\rho_{\infty}(T)}\right)\quad(7.7)
\]

Since \(d\rho_{\infty}(T)/dT\) is always positive, the above formula indicates that a resistivity minimum occurs when \(\rho_{\infty}(T)\), \(D(w)\) and \(A(w)\) fulfill the following condition:
\[ \rho_{\infty}(T_m) = \frac{A(w)C_0}{D(w)} \]  \hspace{1cm} (7.8)

We can see that the critical temperature \( T_m \) increases when the linewidth \( w \) is reduced. At high temperature where \( T > T_m \), the positive TCR value indicates that the scattering from electron inside the grains is the dominant contribution to the wire resistance. However, upon reducing the temperature below \( T_m \), the grain boundary scattering gradually dominates, and thus a negative TCR value is observed. These conclusions are consistent with the data shown in Figure 7.3.

### 7.2.2 Magnetoresistance properties of polycrystalline CrO\(_2\) nanowires

Low-field magnetoresistance (MR) results are presented in Figure 7.4(a), plotted in terms of the percentage:

\[ \text{MR} = \frac{\Delta \rho(H)}{\rho(H = 0)} = \frac{[\rho(H) - \rho(H = 0)]}{\rho(H = 0)} \]  \hspace{1cm} (7.9)

versus the applied magnetic field (0–3 kOe) for polycrystalline CrO\(_2\) wires with different linewidths. Figure 7.4(b) displays the linewidth dependence of the field at which each sample experiences its maximum resistivity. For polycrystalline samples, these field values are equal to the coercive field \( H_c \) for each wire [18]. We will discuss the longitudinal and transverse magnetoresistance data separately in the following.
Figure 7.4. (a) Longitudinal and transverse magnetoresistance curves measured at 77 K, as a function of magnetic field $H$ for polycrystalline CrO$_2$ wires with different linewdths, and (b) the coercive field $H_c$ as a function of the inverse wire width ($1/w$) in the longitudinal and transverse geometries for polycrystalline CrO$_2$ wires.
(i) Longitudinal Magnetoresistance. It is observed from Figure 7.4(a) that the magnitude of MR increases when there is a reduction in the linewidth of the sample. As has been discussed previously, the mean transmission probability \( \Gamma(w) \) decreases with reduced \( w \) due to the fact that the further restriction in the available electron conduction paths causes an increase in the effective grain boundary resistance. Also, it has been reported that annealing the polycrystalline CrO\(_2\) sample in the air increases its magnetoresistance and resistivity, which has been attributed to the partial reduction of CrO\(_2\) into Cr\(_2\)O\(_3\) in the grain boundary regions [82,178]. Thus, it seems clear that the MR value is closely related to the structure of the grain boundaries, with the MR value increasing for smaller \( \Gamma(w) \), which is a direct consequence of reducing the linewidth \( w \).

(ii) Transverse Magnetoresistance. The \( H_c \) in this case shows a much stronger width dependence, following a \( 1/w \) law. This is due to the fact that in magnetic nanowires with linewidths \( w \) comparable to their thickness \( t \), the demagnetizing field \( H_d \) becomes important. In the transverse case, \( H_d \) can be approximated as \( H_d = 4\pi M_s t/w \) [171], and thus the applied field which is required to reverse the magnetization is given by

\[
H_{ex} = H_{c(bulk)} + \frac{4\pi M_s t}{w} \quad \text{…………………………(7.10)}
\]

Hence, the magnetization reversal process becomes much more difficult when the wire width is reduced, with the corresponding coercive field showing a \( 1/w \) behavior. When the external field is set to its maximum value (3 kOe), the wire’s internal field decreases for samples with smaller linewidths. This means that saturating the magnetization of polycrystalline CrO\(_2\) wires in the transverse direction is much more difficult for smaller linewidths \( w \), resulting in a decrease in the MR value, as shown in Figure 7.4(a).
Figure 7.4(b) also shows that for bulk polycrystalline CrO$_2$ films (i.e., $1/w \rightarrow 0$), the coercive fields $H_c$ in the longitudinal and transverse directions are nearly the same. This implies that the polycrystalline CrO$_2$ samples are perfectly isotropic in the plane. However, for epitaxial CrO$_2$ samples, which will be discussed in the next section, the in-plane coercive field is not isotropic.

### 7.3 Epitaxial CrO$_2$ nanowires

Figure 7.5 shows a scanning electron microscopy (SEM) image of two epitaxial (100)-oriented CrO$_2$ nanowires deposited using selective-area growth technique. There are no grains or grain boundaries observed within the wires, indicating that these structures are single crystal. The low temperature transport properties of epitaxial CrO$_2$ nanowires are discussed in the following.

![SEM image of CrO$_2$ nanowires](image)

Figure 7.5. SEM images of two single crystal CrO$_2$ nanowires grown on a (100)-TiO$_2$ substrate. The linewidths of the wires are 100 nm and 200 nm, respectively. The inset shows the enlarged view of the nanowire with 100 nm in width.
7.3.1 Electrical properties of epitaxial CrO$_2$ nanowires

The temperature dependence of resistivity for single crystal CrO$_2$ wires with different crystal orientations and linewidths is presented in Figure 7.6. The resistivity of epitaxial wires is much lower than that of polycrystalline wires, and no resistivity minimum at $T_m$ exists in single crystal wires. This observation further confirms that $T_m$ in polycrystalline CrO$_2$ wire is due to the grain boundary effect. Because very few, if any, grain boundaries are formed in the epitaxial CrO$_2$ wires, the scattering probability of the conduction electrons is dramatically reduced, leading to a much smaller wire resistivity.

Figure 7.6. Resistivity as a function of temperature for epitaxial CrO$_2$ nanowires with different linewidths aligned along the (a) [001] direction and (b) [010] directions. All the wires have a thickness of $\sim$ 100 nm.
Furthermore, upon reducing the linewidth, we can see that for CrO$_2$ wires aligned along the [010] direction (b axis), the resistivity $\rho(w,T)$ increases at any given temperature. From 10 \( \mu \)m to 100 nm, the resistivity jumps by nearly 40 \( \mu \Omega \cdot \text{cm} \), as shown in Figure 7.6. However, regardless of wire width, very small variations were observed in the resistivity plots of the wires whose long axis was parallel to the [001] direction (c axis). The resistivity increases by less than 5 \( \mu \Omega \cdot \text{cm} \) from 10 \( \mu \)m to 100 nm in this case. For epitaxial CrO$_2$ films, band structure calculations have predicted a value of $3.5 \times 10^{-5} \mu \Omega \cdot \text{cm}^2$ for $\rho_{\infty}(T)/\tau(T)$ [15]. Based on Equation 7.5, we find that $\rho_{\text{surface}}(w,T)$ is less than 2.6 \( \mu \Omega \cdot \text{cm} \) for \( w = 100 \) nm, a value which is much smaller than the resistivity changes shown in Figure 7.6(b). Hence, again we can neglect the extra resistivity term due to the surface scattering, when considering the effects of decreasing linewidth \( w \). We attribute this orientational resistivity behavior to the strain anisotropy in the single crystal CrO$_2$ wires, as explained next.

The lattice mismatch between a CrO$_2$ epitaxial film and TiO$_2$ substrate is −3.79% along the [010] axis and only 1.48% along the [001] axis. If we let CrO$_2$ grow freely, it has a preferential lateral growth direction along the [001] axis to achieve less lattice mismatch. For example, selective-area growth of a CrO$_2$ circular dot naturally deform into a rectangular shape with long side parallel to the c axis [26,167]. Therefore, the SiO$_2$ sidewall should produce much more pressure in the transverse direction, an effect which intensifies when reducing the linewidth, for the wires aligned along the b axis. Because higher sidewall pressure tends to generate more lattice defects (scattering centers) inside the CrO$_2$ nanowires, the resistivity of the wire aligned along the b axis can be expected to exhibit a much stronger linewidth dependence; this agrees with the data shown in Figure 7.6.
7.3.2 Magnetoresistance properties of epitaxial CrO$_2$ nanowires

(i) Wires aligned along the [001] direction. Figure 7.7 plots the longitudinal and transverse MR as a function of the applied magnetic field $H$ for epitaxial CrO$_2$ nanowires aligned along the [010] direction. All the measurements were made at 77 K.

It is clear that the [001] direction is the magnetic easy axis for single-crystal CrO$_2$ films with a thickness of 100 nm [17]; additionally, the shape anisotropy also favors a situation where the magnetic moments are aligned in this direction (along the wire axis). Thus, in the longitudinal case, we observe sharp magnetization changes in the CrO$_2$ nanowires, indicated by the resistance drops in Figure 7.7(a). When the field is applied perpendicular to this easy axis, as shown in Figure 7.7(b), the remanent magnetization state for the domains is along the $c$-axis direction. In this case, the magnetic moments rotate almost coherently from this direction to the $b$-axis direction when the magnitude of the transversely applied field is increased, resulting in a gradually decreasing resistivity without any sudden drops.

Figure 7.8 displays the coercive fields $H_c$, as extracted from the data in Figure 7.7 as a function of the inverse linewidth. It is found that the $H_c$ is roughly proportional to the inverse of width: $H_c \sim 1/w$. This behavior is in good agreement with investigations of some other ferromagnetic wires such as Co, NiFe, etc., and can be explained by considering the shape dependence of the stray field of the wire [179,180]. A decrease in linewidth increases the aspect ratio of the magnetic nanowires correspondingly, and results in a higher shape anisotropy, which makes the magnetic states parallel to the wire axis more favorable and more difficult to switch; hence, a higher coercivity $H_c$. 
Figure 7.7. Low-field (a) longitudinal and (b) transverse MR curves of epitaxial CrO$_2$ nanowires aligned along the [001] easy axis direction with different linewidths, measured at 77 K. The schematic drawings above each curve represent the different magnetization states present during the magnetization reversal process.
Unlike the polycrystalline CrO₂ bulk films, we can see that the coercive fields plotted in Figure 7.8 for the two different wire geometries do not approach a single value when extrapolated to the origin. This is due to the fact that the epitaxial [001]-CrO₂ film is anisotropic within the plane because of the two distinct crystal directions. The intrinsic magnetocrystalline anisotropy favors alignment along the [001] easy axis; thus the longitudinal coercivity is larger than the transverse value, even in the limit of large linewidth. The measured longitudinal MR properties of single crystal CrO₂ nanowires aligned along the magnetic easy axis is consistent with the observation of Konig et al [181] for epitaxial CrO₂ wires with width larger than half micron. The difference in the transverse MR behaviors may lie in the different ways of fabricating CrO₂ wires. Additionally, when reducing the linewidth down to 100 nm, another MR behavior is observed for epitaxial CrO₂ wire aligned along the hard axis, which is discussed in the following.

Figure 7.8. Coercive field $H_c$ as a function of the inverse linewidths $1/w$ in both the longitudinal and transverse geometries for single crystal CrO₂ wires with wire axes aligned along the [001] direction.
(ii) **Wires aligned along the [010] direction.** In this case, the magnetic easy-axis direction, preferred by the magnetocrystalline anisotropy term, and the shape anisotropy direction are perpendicular to each other. Therefore, the magnetization behavior of the epitaxial CrO$_2$ wires aligned along the $b$ axis depends on the relative strengths of these two anisotropies. Through MFM studies of epitaxial CrO$_2$ wires [167,26], it has been observed that the shape dependent contribution to the anisotropy is appreciable only for CrO$_2$ nanowires with very small linewidths. For most of the wires, the magnetocrystalline anisotropy dominates over the shape anisotropy, giving the epitaxial CrO$_2$ wires a stripelike domain configuration, with domains either magnetized parallel or antiparallel to the magnetic easy axis direction ([001]) at remanence.

The magnetoresistance behavior of epitaxial CrO$_2$ wires along the $b$ axis is shown in Figure 7.9. The MR curves display more features than those [001] wires in Figure 7.7. These more complex curves are the consequence of diverse types of magnetic domain patterns formed in the [010] wires. Figure 7.9 also shows the schematic pictures of various domain patterns at some specific magnetic states, which are inferred from the MR curves and the competitive anisotropies.

It is seen that the MR response of the smallest wire ($w=100$ nm) differs significantly from the wires with larger widths (350 nm and more). The narrowest wire exhibits MR behavior similar to that measured for wires aligned along the $c$ axis, as shown in Figure 7.7. This suggests that a similar magnetization reversal process exists, and the remanent magnetic state is dominated by the shape anisotropy, leaving the remanent magnetization nearly parallel to the wire axis. When the linewidth increases, the shape induced
Figure 7.9. Low-field (a) longitudinal and (b) transverse MR curves of epitaxial CrO$_2$ nanowires with different linewidths. The wires are all aligned along the [010] hard axis direction and are measured at 77 K. Schematics at the top of each figure represent the different magnetization states which occur during the reversal process.
contribution decreases and the effects of the magnetocrystalline anisotropy become more important.

In the longitudinal case shown in Figure 7.9(a) (e.g., 350 nm width), at high negative fields (-2 kOe), nearly all the magnetic moments are aligned along the wire axis, resulting in a minimal wire resistance. As the field is reduced to zero, a complicated magnetic domain structure emerges. Biehler et al [169] found that, compared with the stripe domain structure obtained after initial saturating along the easy axis, this remanent state, which is formed after initial saturating along the hard axis, shows narrower domain widths because some domains do not extend across the whole wire width and the magnetization vectors in the neighboring domains are canted. Therefore, the sample resistance reaches a maximum value near zero field due to the increase in the number of domain walls.

Upon further increasing the external field in the positive direction, the stripe domain structure is formed, resulting in a lower resistance. Later on, the magnetic field is large enough to break the stable stripe domain structure, by forming extra domain walls, and this is the reason for the second resistance peak near 1 kOe in Figure 7.9(a). A final decrease in the resistance is observed due to the formation, in sufficiently large fields, of a nearly single domain structure with magnetization parallel to the wire axis. A similar MR behavior has been reported recently for epitaxial CrO2 wire with 2 µm width [181].

In Figure 7.9(b), the magnetic field is applied in the transverse direction, which is also the direction of the magnetic easy axis. At large negative applied fields, nearly all the magnetic domains are aligned in the external field direction ([001]). Upon decreasing the field value, some of the domains split into multiple smaller ones with different magnetization directions in order to minimize the total magnetic energy. In this intermediate state,
the increase in domain wall scattering leads to a higher wire resistance. As the field approaches zero, these multiple domains recombine and the whole wire stabilizes in the aforementioned stripelike domain structure, which causes a reduction in the number of domain walls and leads to the resistance valley near zero field. Furthermore, we can see that this resistance valley becomes less pronounced as a wire narrows, and finally disappears for very narrow wires. This can be understood by considering that the shape induced effects are gradually becoming important, as the linewidth is decreased, making the stripe-like domain structure, which is preferred by the magnetocrystalline anisotropy, less stable.

Overall, the magnetoresistance values measured for single crystal CrO$_2$ nanowires are smaller than those of polycrystalline nanowires by more than a factor of 10. This suggests that magnetic scattering at the grain boundaries is much stronger than the scattering which occurs at the domain walls.

### 7.4 Summary

In conclusion, we have studied and compared the electrical resistivity and magnetotransport properties of both polycrystalline and epitaxial CrO$_2$ nanowires grown under the same conditions by chemical vapor deposition using the selective-area growth technique. A transition of the temperature coefficient of resistivity from positive to negative values is observed for polycrystalline nanowires, and the magnitude of the resistivity increases as the linewidth of the wires is reduced. Analyzing the resistivity data using a model of grain boundary scattering indicates that the bulk resistivity of CrO$_2$ nanograins is
much larger than the values reported for single crystal CrO$_2$ bulk films, and this discrepancy is attributed to strain-induced defects. Resistivity measurements also show that epitaxial CrO$_2$ nanowires have a generally metallic character, with some anisotropy observed in the resistivity of the wires aligned along the $b$- and $c$-axis directions. When the linewidth of polycrystalline CrO$_2$ wires is reduced, the longitudinal MR ratio increases, due to changes in the electron conduction paths. A decrease in the transverse MR values for decreasing linewidth results from an increase in the shape-dependent demagnetizing field. Unlike the polycrystalline wires, the MR properties of single-crystal CrO$_2$ wires are strongly dependent on the crystal orientations of the wires, because in addition to the expected shape-induced effects, the magnetocrystalline anisotropy also plays a very important role. Our result shows that the field-dependent magnetic domain structures evolve in a complex fashion, particularly for wires that form stripelike domains at zero field. By taking advantage of the competing magnetocrystalline and shape anisotropies, one can design certain CrO$_2$ epitaxial nanostructures with unique magnetic domain structures, which can lead to interesting spin-dependent transport behavior.
Chapter 8

Large Single Domain Wall Resistance in Epitaxial CrO$_2$ Nanocontacts

We have studied magneto-transport properties of half-metallic epitaxial chromium dioxide (CrO$_2$) nanoscale continuous contacts. Manipulating the domain walls using a large dc current in the contact area yields a magnetoresistance of up to 25%, which is the largest ever seen in a single ferromagnetic film. The single domain-wall-resistance (DWR) is determined to be three orders of magnitude larger than that of conventional 3$d$ ferromagnets, as a result of the material's half-metallicity. We have measured DWR and the spin-torque effect along different crystallographic axes and at varying temperatures. Finally, we present the results of a theoretical analysis of this system, based on its half-metallic character and on the intrinsic magnetic behavior of CrO$_2$. 
8.1 Introduction

Research into spintronics has improved our understanding of spin-dependent transport in heterogeneous structures [182,183]. Over the past decade, giant magnetoresistance (GMR) and magnetic tunneling junction (MTJ) [5,46] devices have been increasingly integrated into commercial applications. However, it is possible that current spintronics research may lead to new generations of electronic devices with enhanced performance over existing ones. Currently, applications based on magnetoresistive structures have tended to utilize highly complicated multilayered designs. The ability to achieve large magnetoresistive effects in a structure consisting of a single nanoscale ferromagnetic element would have numerous benefits; most importantly, it would make lateral spintronic devices possible and their manufacturing feasible. With this objective in mind, we have been exploring the magnetotransport behavior across a single magnetic domain wall in epitaxial half-metallic systems where conduction electrons are fully spin-polarized. We believe that the domain-wall resistance (DWR) in these films may become the foundation of future generations of spintronic devices.

In this Chapter, we report an extremely large single-magnetic-domain wall resistance (DWR) in epitaxial CrO$_2$ nanocontacts. The domain-wall resistance-area (RA) product is three orders of magnitude larger than what has been measured in Co and NiFe nanostructures [184]. We measured the DWR by using current-driven magnetization switching (the spin-torque effect). We interpret the large DWR as a result of CrO$_2$'s half-metallicity and the single crystal nature of the structures. We also have observed a strong crystalline orientation effect and a large thermal effect on spin torque, as well as an unusually large switching current density.
8.2 Experimental procedure

Chromium dioxide is the only material which has been unambiguously confirmed as a half-metal with complete spin-polarization by both theoretical modeling [15] and many experimental methods [11,6]. We have grown high quality CrO₂ epitaxial films using atmospheric chemical vapor deposition (CVD) with chromium trioxide (CrO₃) as a precursor [79]. In order to grow lateral epitaxial CrO₂ nanocontacts, we have adopted a selective-area growth technique. In this method, an arbitrary nanostructure is grown during CVD without the need for any post-deposition patterning (ion-milling, chemical etching, or lift-off, etc.), thus avoiding any structural defects caused by such processes. On a (100)-TiO₂ substrate, we deposited an amorphous SiO₂ film and patterned it using electron-beam lithography into a given shape, where a nanocontact window was opened to expose the TiO₂ substrate [26,167]. We then formed the CrO₂ nanocontact by taking advantage of the fact that CrO₂ has zero sticking coefficient on SiO₂ but a high affinity for the TiO₂ substrate. On each substrate, we fabricated a series of CrO₂ nanocontacts with their symmetry axes oriented along various crystalline directions.

8.3 Results and discussion

Figure 8.1 is a scanning electron micrograph (SEM) of an epitaxial CrO₂ nanocontact with a 30 nm constriction and a symmetry axis along the [001] direction (which is the magnetic easy axis). We will refer to these kind of samples as easy-type, and samples oriented along the [010] hard-axis as hard-type. Electrical current was applied along the [001] direction. The two small probes (not shown) on either side of the contact are integral parts of the sample with a distance of 3 µm between them. We measured the dc resistance
Figure 8.1. False-colored SEM image of an epitaxial CrO₂ nanocontact structure on a (100) oriented TiO₂ substrate. The contact is 30 nm wide and 80 nm thick. It is aligned along the [001]-axis, which is also the magnetic easy axis of single crystal CrO₂.

\( V/I \) of the samples in a liquid nitrogen cryostat using a conventional four-probe method without any external magnetic field.

Figure 8.2(a) shows the resistance of an easy-type [001] nanocontact as a function of current at 77 K. When the applied current is increased to above a critical current \( I^{(1)}_c = 6.7 \text{ mA} \), the nanocontact resistance drops precipitously to a new value (from state A to B). The magnitude of the resistance drop \( \Delta R = R_A - R_B \) is 54 Ω, which corresponds to a change in resistance of \( \Delta R/R_B \sim 25\% \). Furthermore, a clear hysteresis loop is observed when the current sweeps back from above \( I^{(1)}_c \) to below a second critical value \( I^{(2)}_c = 5.9 \text{ mA} \). For this system, the current coercivity \( \Delta I_c = I^{(1)}_c - I^{(2)}_c \) is 0.8 mA. Figure 8.2(b) shows the corresponding result for a hard-type [010] nanocontact. Qualitatively, the current-driven resistance switching and the hysteretic behavior are similar for both types of samples. However,
Figure 8.2. Resistance versus dc current for epitaxial CrO$_2$ nanocontacts aligned along the (a) [001]-direction (easy-type) and (b) [010]-direction (hard-type).

The hard-type sample displays a smaller resistance change (10% versus 25%) and a smaller current coercivity (0.2 mA versus 0.8 mA).

We can exclude with certainty the effects of local heating in trying to understand the results in Figure 8.2. Joule heating induces a negligible positive shift in $R$ when the...
resistance jumps back to its original value at $I^{(2)}_c$. Furthermore, a comparison with the temperature dependence of resistivity of epitaxial CrO$_2$ [18,185] allows us to estimate the sample heating at no more than 1 K. Additionally, any heating effect should increase the sample resistance while our measurements actually show sharp resistance drops, and the switching process is highly reproducible. Therefore, we can conclude that the data in Figure 8.2 are the result of magnetic effects.

Figure 8.3 shows the Magnetic Force Microscopy (MFM) images of both types of nanocontacts in the remanent state. For the easy-type contact in Figure 8.3(a), two strong magnetic poles exist in the contact region. As schematically shown in Figure 8.3(c), a small magnetic domain trapped in the contact region opposes the two large neighboring magnetic domains away from the contact. This state (State A) remains intact until the current is increased above the critical value $I > I^{(1)}_c$ at which point a new, uniform state is realized, i.e. the State B in Figure 8.3(e).

On the other hand, the remanent state for the hard-type nanocontact, as shown in Figure 8.3(b) and 8.3(d), consists of stripe-like domain structures which are formed beside the constricted area with no obvious magnetic poles observed in the contact region. In this case, the magnetic easy-axis direction ([001]), preferred by the magnetocrystalline anisotropy energy term, is orthogonal to the shape anisotropy direction ([010]). Normally, the magnetocrystalline anisotropy would dominate, however, when the dimension of CrO$_2$ structure falls below 100 nm, the magnitude of both anisotropies is comparable [186,24]. Thus, the magnetic moments in the constriction are expected to be canted with respect to those in the neighboring domains, as indicated in Figure 8.3(d). Above $I^{(1)}_c$, this canted spin state is eliminated, i.e. the State B in Figure 8.3(f).
Figure 8.3. MFM images of CrO$_2$ nanocontacts in the remanent state: (a) easy-type and (b) hard-type. The most probable domain configurations with current less than $I_{c}^{(1)}$: (c) easy-type and (d) hard-type. Domain configurations with current larger than $I_{c}^{(1)}$: (e) easy-type and (f) hard-type. The arrows in (a) and (b) point to the magnetic poles.
A small domain might be trapped in the contact region for two reasons. First, due to the spontaneous magnetization DW(s) may exist in the constricted area of a ferromagnetic nanocontact structure when the contact width is narrow enough [24,25]. Secondly, the lattice mismatch between CrO$_2$ and TiO$_2$ induces a large strain which may not be fully relaxed in the contact region. Also, stress from the SiO$_2$ sidewalls which confine the lateral growth of CrO$_2$ can further amplify the strain [185]. Both types of strain can act as a pinning force for domain walls.

As predicted by Berger [128] and confirmed experimentally [187], domain walls can be displaced under the influence of a spin polarized current. This effect is due to the exchange torque exerted by electrons in the conduction band on the constituent electrons of the domain wall. The net effect is a displacement of the domain wall in the same direction as that of the current carriers, known as current-induced s-d exchange interaction. The difference between the two resistance states is, therefore, attributed to the removal of the domain wall from the constriction at a large critical current density. In the low resistance state, no domain wall from the constriction is pinned at presence of a domain wall must be responsible for the additional resistance observed. Thus, the difference between the two states can be used to obtain a direct measurement of the domain wall resistance, without the use of an applied magnetic field.

Figure 8.3(e) and 8.3(f) display the domain structure of epitaxial CrO$_2$ nanocontacts under the influence of a large current ($I > I_c$). In state B, the domain magnetization in the contact area is forced to be aligned with its neighboring domains due to the spin transfer torque effect. The removal of the domain walls reduces the spin-dependent scattering, and hence increases the conductance in the constricted area.
Based on this analysis, we can calculate the resistance-area product (RA) for the domain walls, assuming one domain (i.e. two DWs) is trapped in the easy-type [001] CrO₂ nanocontact. From the value of $\Delta R = 2 \times R_{DW}$ and experimental cross-sectional area of $30 \times 80$ nm$^2$, we find that a single DW has an RA of $0.65 \times 10^{-13}$ $\Omega$·m$^2$ at 77 K, which is three orders of magnitude larger than the values reported for 3d ferromagnets (Co and NiFe [184]). We attribute this giant domain wall resistance-area product value to the half-metallicity of chromium dioxide based on the following analysis.

As stated in previous Chapters, Levy and Zhang [94] proposed a model to explain the domain wall resistance and found that the resistance change ratio $\Delta R/R$ can be expressed as:

$$\frac{\Delta R}{R} = \frac{\xi^2}{5} \left( \rho_0^+ - \rho_0^- \right)^2 \left( 3 + \frac{10\sqrt{\alpha}}{\rho_0^+ \rho_0^-} \right)$$

$$= \frac{\xi^2}{5} (\alpha - 1)^2 \left( 3 + \frac{10\sqrt{\alpha}}{\alpha + 1} \right)$$

with $\alpha = \rho_0^+ / \rho_0^-$

In the preceding equation, $\xi = \hbar^2 k_F/16\pi m_e d J$, where $k_F$ is the Fermi wave vector, $m_e$ is the effective mass, $d$ is the domain wall width and $J$ is the Stoner exchange splitting. The spin asymmetry of the current is given by $\alpha = \rho_0^+/\rho_0^-$, which depends on the relative resistivities $\rho_i^{(\uparrow)}$ of the spin-up(down) channels.

Applying this model to chromium dioxide, we estimate that the domain wall width $d_{DW} = 2\sqrt{J/K} = 26$ nm, where the exchange stiffness constant $A = 4.6 \times 10^7$ erg/cm$^3$ and $K = 2.6 \times 10^5$ erg/cm$^3$ [17]. Furthermore, with $k_F \sim 1$ Å, $J \approx 1.8$ eV [15] and a single DWR ratio $\Delta R/2R = 12\%$, we find a $\alpha = \rho_0^+/\rho_0^-$ ratio on the order of $10^3$ for epitaxial CrO₂. This
extremely large spin-asymmetry ratio indicates that the density of spin-up carriers is much larger than that of spin-down carriers in CrO$_2$ at low temperature, which is in excellent accordance with the expected half-metallicity of this material.

Figure 8.4 show the RA and magnetoresistance (MR) versus temperature for an easy-type nanocontact sample. Both quantities decrease with increasing temperature and

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**Figure 8.4.** Temperature dependence of (a) resistance-area product and (b) resistance change ratio $\Delta R/R$ for an easy-type nanocontact sample.
become effectively zero for $T > 200$ K, which is significantly less than the transition temperature $T_c = 395$ K [18]. In Zhang’s model, this result can be interpreted as resulting from the reduction of the spin-asymmetry ratio $\alpha = \rho_0^\uparrow/\rho_0^\downarrow$ as $T$ rises. In other words, the half-metallicity of CrO$_2$ is susceptible to increasing spin-flip scattering at higher temperatures. Additionally, the smaller anisotropy constant $K$ at higher temperatures will increase the domain wall width $d_{DW}$, which in turn would also reduce the DWR (smaller $\xi$).

![Figure 8.5. Temperature dependence of (a) critical current density $I_c$ (jump up and jump down) for an easy-type nanocontact sample, and (b) current coercivity $\Delta I_c$ for CrO$_2$ nanocontact (easy-type and hard-type).](image)
Figure 8.5 show the switching current $I_c$ and current coercivity $\Delta I_c$ versus temperature, respectively. Both quantities decrease with increasing temperature, which can be understood by considering the effects of thermal activation. For a thermally activated switching process with an effective energy barrier $E_a$, the average spin-torque reversal current can be written as [188]:

$$I_c = I_{c0} \left[ 1 - \frac{k_B T}{E_a} \ln \left( \frac{k_B T |I_{c0}|}{\tau_0 E_a |R_f|} \right) \right]$$

where $I_{c0}$ is the intrinsic critical switching current without thermal fluctuations, $\tau_0$ is the characteristic fluctuation attempt time and $R_f$ is the ramp rate for current. In our experiment, $R_f = 0.01$ mA s$^{-1}$ and $\tau_0$ can be assumed to be 1 ns, giving best fit values of $I_{c0}^{(1)} = 8.46$ mA, $E_a^{(1)} = 0.66$ eV for $I_c^{(1)}$, and $I_{c0}^{(2)} = 7.37$ mA, $E_a^{(2)} = 0.75$ eV for $I_c^{(2)}$. The obtained energy barrier is much smaller than the values (a few eV) obtained for GMR devices. This can be partially explained by considering the extra barrier formed by the non-magnetic spacer layer in GMR structures. Furthermore, there is a small difference between $E_a^{(1)}$ and $E_a^{(2)}$, which has been attributed to the different magnitude of perturbations felt by the domain (due to neighboring domains), in the parallel and antiparallel states [188]. Finally, the larger current coercivity at lower temperatures is caused by the enhanced magneto-crystalline anisotropy in CrO$_2$.

Figure 8.6 shows $\Delta R/R_B$ and $\Delta I_c$ of nanocontacts measured along different crystalline directions. Both quantities are at their largest for the easy-type [001] samples and smallest for the hard-type [010] samples. Partly, this is because the easy-type nanocontact has much sharper DWs than the hard-type, as can be seen in Figure 8.3. The 180-degree...
magnetization transition across the DW in the easy-type samples tends to yield a larger RA. Furthermore, in the case of the easy-type samples, the shape anisotropy is aligned in the same direction as the magnetocrystalline anisotropy which makes the energy barrier between state B and state A larger than the corresponding hard-type transition. Thus, a higher current coercivity $\Delta I_c$ was observed. Moreover, the band structure of CrO$_2$ may also play a large role in the aforementioned crystallographic dependence.

Figure 8.6. (a) Magnetoresistance ratio $\Delta R/R_B$ and (b) current coercivity $\Delta I_c$ of CrO$_2$ nanocontacts as a function of the crystallographic angle $\theta$, with respect to the magnetic easy axis direction [001], at 77 K.
Finally, we can estimate that the current density $J_c$ required to switch the resistance is of the order $10^8$ A/cm$^2$. This value is unexpectedly larger than what is reported for Ni, Fe and other ferromagnetic nanocontacts [24,25]. By solving the Landau-Lifshitz-Gilbert equation with the macrospin approximation [189,190], the critical current $I_c$ for spin-torque driven magnetic reversal in a monodomain nanomagnet without external magnetic field applied is given by:

$$I_c = \left(\frac{2e}{\hbar}\right)\left(\frac{\alpha}{P}\right) VM_s \left(H_k + 2\pi M_s\right)$$

where $\alpha$ is the Gilbert damping coefficient, $P$ is the spin-polarization of the current, $V$ is the volume of the domain, $H_k$ is the anisotropy field and $M_s$ is the saturation magnetization. If we assume the length of the domain to be 50 nm, then the value of $I_c/V$ is about $0.2 \times 10^{14}$ A/cm$^3$. With $P = 1$, $M_s = 640$ emu/cm$^3$ and $H_k = 800$ Oe for bulk CrO$_2$ thin films at 77 K, the Gilbert damping coefficient $\alpha$ is determined to be around 0.02, which is almost 10 times larger than the value of 0.0023 measured at 300 K in unpatterned CrO$_2$ thin films by ferromagnetic resonance (FMR) [191]. Although spin pumping could play a role, and magnetic damping effect is dependent on the temperature and magnetic configuration [192], this huge variation suggests there are other factors responsible for the enhancement of the damping coefficient, which we attribute to the existence of a decomposed Cr$_2$O$_3$ layer on the surface of the CrO$_2$.

Cr$_2$O$_3$ is antiferromagnet (AF) with a Neel temperature $T_N = 307$ K [193], and a layer of Cr$_2$O$_3$ always occurs on the surface of CrO$_2$ because it is thermodynamically a more stable state. The fraction of Cr$_2$O$_3$ in the constricted region is also increased due to an increased surface-to-volume ratio in the constricted area of the CrO$_2$ nanocontact. Fur-
thermore, an enhancement in the Gilbert damping has been previously reported in FM/AF bilayers such as NiFe/NiO [194,195] and Co/CoO [196]. In these reports, the measured damping value can be several times larger than that of the pure FM film and the damping is observed to increase with decreasing FM film thickness. This effect can be explained by a relaxation mechanism based on two-magnon scattering arising from local fluctuations of interfacial exchange coupling. Thus, exchange biasing in the CrO₂/Cr₂O₃ bilayer at the constricted region could significantly increase the damping coefficient, which directly increases the critical switching current. On the other hand, a broadening of the anisotropy field of \( H_k \) in CrO₂/Cr₂O₃ bilayers also yields a higher \( I_c \).

### 8.4 Summary

In conclusion, we have measured the single magnetic domain wall resistance (RA) in epitaxial CrO2 nanocontacts. The obtained RA is three orders of magnitude larger than conventional ferromagnets, a direct consequence of the chromium dioxide's half metallicity. The current-induced spin torque effect and RA show a strong dependence on crystalline orientation and temperature. The naturally decomposed Cr₂O₃ on the surface of the CrO₂ is found to be responsible for the unusually large switching current density through the exchange coupling, which significantly increases the Gilbert damping coefficient. Our results demonstrate that single crystal half-metals can exhibit enhanced magneto-transport effect across domain walls, which may be applicable in future’s spintronic devices based on magnetic domain wall motion.
Chapter 9

Conclusion

In this thesis, we present a new method, based on the selective-area growth technique, to fabricate chromium dioxide (CrO$_2$) nanostructures. This way avoids the need to pattern the CrO$_2$ thin film after deposition (such as using wet etching, RIE and FIB) and, hence, prevent the subsequent degradation of the film to a more stable chromium oxide Cr$_2$O$_3$. Both high quality polycrystalline and single crystal CrO$_2$ nanostructures with individual feature size smaller than 80 nm can be readily obtained with this method.

The morphological study shows that the polycrystalline nanostructures are composed of many CrO$_2$ grains with different orientations, and neighboring grains are separated by very thin grain boundaries. Multiple grains are observed to form in the polycrystalline CrO$_2$ nanodots with diameter larger than 100 nm, however, below which only a single grain is allowed to exist. On the contrary, no obvious grains and grain boundaries are observed in epitaxial CrO$_2$ structures. The anisotropy induced by the lattice mismatch can be directly inferred from the rectangular shape of the single crystal CrO$_2$ nanodots, which
have their long side parallel to the $c$ axis. This can be attributed to the difference in the lattice constant mismatch between CrO$_2$ and the TiO$_2$ substrate for the $b$ and $c$ axes. Furthermore, the application of pre-patterning allows us to study the nanocrystal growth process during chemical vapor deposition. The lateral overgrowth rate of epitaxial CrO$_2$ nanocrystals is found to be highly anisotropic, which is affected by both the crystallographic orientation and the deposited thickness, and finally maximized at the [011]-direction of the TiO$_2$ substrate.

We have investigated the domain configuration and magnetic reversal process of several CrO$_2$ patterns grown epitaxially on (100)-TiO$_2$ including nanodots, nanowires, and ring structures using magnetic force microscopy. The in-plane, stripelike, domain structures with domain walls aligned mainly along the [001] direction indicate a strong magnetocrystalline anisotropy, which makes the shape anisotropy contribution almost negligible. We have also found that all the domains tend to have a similar aspect ratio. This can be understood with a classical model for uniaxial magnetic films, and estimates of the domain wall energy density and exchange stiffness constant for CrO$_2$ were obtained. Moreover, a strong dependence of the magnetic reversal process on the geometrical size of the CrO$_2$ elements is observed.

We have also studied and compared the electrical resistivity and magnetotransport properties of both polycrystalline and epitaxial CrO$_2$ nanowires grown under the same conditions. A transition of the temperature coefficient of resistivity from positive to negative values is observed for polycrystalline nanowires, and the magnitude of the resistivity increases as the linewidth of the wires is reduced. Analyzing the resistivity data using a model of grain boundary scattering indicates that the bulk resistivity of CrO$_2$ nanograins is
much larger than the values reported for single crystal CrO₂ bulk films, and this discrepancy is attributed to strain-induced defects. Resistivity measurements also show that epitaxial CrO₂ nanowires have a generally metallic character, with some anisotropy observed in the resistivity of the wires aligned along the b- and c-axis directions. When the linewidth of polycrystalline CrO₂ wires is reduced, the longitudinal MR ratio increases, due to changes in the electron conduction paths. A decrease in the transverse MR values for decreasing linewidth results from an increase in the shape-dependent demagnetizing field.

Unlike the polycrystalline wires, the MR properties of single-crystal CrO₂ wires are strongly dependent on the crystal orientations of the wires, because in addition to the expected shape-induced effects, the magnetocrystalline anisotropy also plays a very important role. By studying the MR curves, we inferred the internal magnetic domain structures in various single crystal CrO₂ wires and found that the spin-dependent transport is much stronger across a grain boundary than a magnetic domain wall.

Finally, we have measured the single magnetic domain wall resistance in epitaxial CrO₂ nanocontact structures. Manipulating the domain wall using a large dc current in the nanocontact region yields a magnetoresistance of up to 25%, which is the largest ever seen in a single ferromagnetic film. The obtained domain wall resistivity (RA) is three orders of magnitude larger than conventional ferromagnets (such as Ni, Fe and Co), as a direct consequence of the chromium dioxide's half-metallicity. The current-induced spin transfer torque effect and RA show a strong dependence on crystalline orientation and temperature. Furthermore, the naturally decomposed Cr₂O₃ on the surface of the CrO₂ is found to be responsible for the unusually large switching current density through the exchange coupling, which significantly increases the Gilbert damping coefficient.
Our results shows that by taking advantage of the competing magnetocrystalline and shape anisotropies, one can design certain CrO$_2$ epitaxial nanostructures with unique magnetic domain structures, which can lead to interesting spin-dependent transport behavior. We also demonstrate that single crystal half-metals can exhibit enhanced magnet-to-transport across domain walls, and this property opens up new avenues for spintronics applications based on magnetic single domain wall devices.
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