Engineering Magnetic Domain Walls in Magnetic Nanowires

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Abstract

Domain wall manipulation in ferromagnets shows great promise for the development of fast and efficient computer memory devices. In particular, chromium dioxide has a half-metal characteristic that holds the potential for reducing the heat produced from reading or writing memory bits. To reliably control the motion of domain walls, CrO$_2$ nanowires are created with geometric anisotropy that acts as a potential well to "pin" domain walls to fixed sites. Each wire was grown using selective-area growth to avoid the creation of random pinning sites from crystal disorder. This process is sensitive to many different factors in the creation of the SiO$_2$ mask. Different effects can interfere with each other, including the proximity effect from electron beam lithography and a sensitivity to the levels of oxygen in the doped SiO$_2$. This thesis presents methods of correction for individual effects, as well as initial results of domain wall mechanics in CrO$_2$ nanowires. Using MFM measurements, I show the static pinning of a domain wall at the predicted pinning location. Magnetoresistance measurements of CrO$_2$ wires ranging from 700 nm to 900 nm wide show that, at this scale, the dominant influence on the domain wall mechanics remains the magnetocrystalline anisotropy, instead of shape anisotropy as desired.
Chapter 1

Introduction

The developing field of spintronics uses the spin of electrons to find effects not seen in conventional electronics that only use the charge. In particular, a current when passed through a ferromagnet becomes spin-polarized. This leads to effects like giant magnetoresistance (GMR), which shows a large change in resistance between two ferromagnets depending on their relative magnetization.

The spin-dependent properties and mechanics are of obvious interest to the memory devices - two ferromagnets with aligned or anti-aligned magnetization translates into a 0 or 1 bit. One of the newest types of memory device currently in development, the so-called “racetrack” memory (RM), uses the domain wall in a nanomagnet as an information storage unit. Unlike RAM or HDD memory, RM has the potential to store multiple bits in a single nanowire (width <1 μm) which enhances the info storage capacity many fold (See Fig. 1.1). RM would function by pushing a whole memory sequence along the wire while read/write elements remain stationary, which could greatly improve the speed of such a device compared to other current memory storage systems [1].

As it stands now, RM has limitations hindering further development. Conventional ferromagnets require a high current to push magnetic domains. High current density in a wire can result in rapid heating, possibly melting the wire or destroying the ferromagnetic state and the information stored within. To continue the development of RM, there is a need to find a suitable ferromagnetic material with sufficiently low critical current density.

Crystal defects or disorder in a wire (e.g. grain boundaries, dislocations, etc.) can drastically increase the threshold current density required to move a DW. At the nanometer scale, defects can cause the motion of
domain boundaries to be erratic in a wire-specific signature. Clean crystal growth is needed to ensure reliable motion and manipulation.

For both these considerations, chromium dioxide is a good candidate. Due to its half-metal band structure, CrO$_2$ has 100% spin-polarized current [2]. This is expected to both decrease the critical current and increase domain wall resistance area product significantly [3]. Recently, high quality faceted CrO$_2$ nanostructures have been fabricated using selective area chemical vapor deposition [4].

Additionally, CrO$_2$ has been shown to carry a large supercurrent in a Josephson junction configuration over long distances of 800nm [5]. It is not yet known how a supercurrent would interact with a magnetic domain boundary; however, the possibility to use a supercurrent to push magnetic domains is worth investigating. If a supercurrent could be used in RM, the device could operate with no heating of the wires at all. It would be possible to decouple the effect of heating and the spin-torque on domain wall dynamics.

![Figure 1.1](image.png)

**Figure 1.1:** Schematic representation of RM memory. The sequence of bits (red and blue) can be pushed along the track past a reading or writing element. Stationary elements allows for effective 3D storage, overcoming one of the major shortcomings of RAM memory. Image from [1]
Chapter 2

Theory of Domain Walls

2.1 Ferromagnetism

A ferromagnet forms when electron spins in a material align. The spin-interaction of the electrons lowers the energy of the system, with the Heisenberg Hamiltonian taking a form

\[ H(\sigma) = - \sum_{i,j} J_{ij} \sigma_i \cdot \sigma_j - h \sum_i \sigma_i, \]  

(2.1)

where \( i, j \) are spins in the system, \( J \) is the interaction energy, and \( h \) is an external field. For a ferromagnet, \( J \) is positive. When the material is cool enough, the initial state spontaneously occurs (equal probability of spin up or spin down states), but can also be influenced by applying an external magnetic field. Below the threshold Curie temperature, there is an imbalance in the number of spins in spin up and spin down states, leading to a net magnetic moment. This magnetic moment adds to an internal magnetic field which self-reinforces so that number of spins in the equilibrium state remains constant.

This internal field splits the electron bands of the material. The spin-up and spin-down states experience a change in energy depending on the alignment of the spins with the field (See Fig. 2.1a). An external fields applied to the material can increase or decrease this difference. With a strong enough field (called the switching field), the energy difference of the bands reverses, leading to a change in the direction of magnetization. Even after the field is turned off, the magnetic moment will remain reversed as a new equilibrium is reached.

Inside the material itself, spins cluster together to form regions with a local magnetic moment different that that of the overall material. These
The presence of a magnetic field splits the spin up and spin down bands. The Fermi Energy level remains constant, leading to a greater number of electron in one band. (b) The two types of domain walls found in a nanowire. (c) The two paths an electron current can take. Within the ferromagnet, majority and minority spins experience different resistances, analogous to parallel resistors drawing different amounts of current. When there is no domain wall, majority spins experience lower resistance (small resistors along the length of the wire). With a domain wall inserted in the middle, the resistances swap for both bands. The majority band has a small resistance along the first half of its path, and a large resistance along the second half, and vice versa for minority spins. Image modified from [3].

Figure 2.1: (a) The presence of a magnetic field splits the spin up and spin down bands. The Fermi Energy level remains constant, leading to a greater number of electron in one band. (b) The two types of domain walls found in a nanowire. (c) The two paths an electron current can take. Within the ferromagnet, majority and minority spins experience different resistances, analogous to parallel resistors drawing different amounts of current. When there is no domain wall, majority spins experience lower resistance (small resistors along the length of the wire). With a domain wall inserted in the middle, the resistances swap for both bands. The majority band has a small resistance along the first half of its path, and a large resistance along the second half, and vice versa for minority spins. Image modified from [3].

regions—called domains—form as a means of optimizing the energy cost from neighboring anti-parallel spins by minimizing the surface area of the boundary between domains. Domains can form naturally when a material transitions to a ferromagnetic state, due to the randomness inherent in the process. They can also be induced in a ferromagnetic by applying a local magnetic field to change the magnetization of some, but not all, of the ferromagnet.

Two relevant energies determine the size and type of the domain wall (DW), namely, exchange and magnetostatic energy. The exchange energy is minimized by the spins’ alignment. In a domain wall, a gradual rotation of the magnetic moment means that no adjacent spins have a large angle between them. Thus, the exchange energy broadens the width of a domain wall. For the domain wall to have finite width, the exchange energy must balance with the magnetostatic energy. The magnetostatic energy arises from Maxwell’s equations, and is the energy cost of magnetic poles, both on the surface from magnetic fields leaving the material (“stray fields”), and in the bulk volume. This acts to decrease the width of the domain wall. The final width of the domain wall depends on the contributions from
both these energies, which changes depending on the material, geometry of the ferromagnet, and type of domain wall present.

In a 2D system, the shapes, magnetizations, and locations of domains are random. Shrinking the system to 1D (wire width < 500 nm), domains form only along the length of the system (not the width), and form directly at 180° angles to each other. In this situation, the domain wall takes one of two forms, shown in Fig. 2.1b. In narrow nanowires transverse domain walls form. The intermediate magnetic moment of the domain wall is perpendicular to the wire axis and the local magnetic moment sweeps across the range of angles in between. When the width of the wire is sufficiently large, a vortex domain wall may form instead. In a vortex domain wall, the magnetic moment forms a vortex. Here, the vortex balances the magnetic poles, minimizing the magnetostatic energy at the cost of increasing the exchange energy [6].

2.1.1 Resistance

It is well-established that resistance in a metal depends on the shape of the band at the Fermi Energy level and the number of electrons available for conduction. In a ferromagnet, this leads to the polarized current. The two different electron bands act analogous to resistors in parallel— one for spin up current, and one for spin down. Current divides between the two electron bands, with more current flowing through the low-resistance majority band (See Fig 2.1c).

A domain wall along the path of the current leads to an increased resistance. Once the current passes the domain wall, the band structure changes, reversing majority and minority bands. Instead of some electrons experiencing a lower resistance, all electrons now feel the increased resistance of being a minority spin for part of the path. Additionally, the change in the band structure leads to electron scattering off the domain wall. The change in resistance depends on the relative resistances of both majority and minority spins and the polarization of the current. With a higher current polarization, the change in resistance becomes more drastic. Therefore, the change in resistance can be used to determine the presence or lack of a domain wall along a section of wire. In the context of RM, the resistance-area (RA) product is the relevant quantity of interest (inverse of conductance per unit area).
2.1.2 Magnetoresistance

Since an external magnetic field shifts the electron bands relative to each other, the shape of the band at the Fermi energy level also changes for both majority and minority spins. This causes a change of the resistance for both spin up and spin down electrons, that change independent of each other. This effect is encapsulated in the magnetoresistance (MR), defined by

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

which looks at the overall resistance of the ferromagnet [3]. MR changes depending on the magnitude of the applied field, the relative orientation of field to the magnetization, and the relative orientation of the field to the current direction. This arises from the scattering of electrons into different orbitals [6]. This effect is called the anisotropic magnetoresistance (AMR).

2.2 Anisotropy and Domain Wall Pinning

Any violation of spatial symmetry carries with it the potential to create anisotropic properties in a material. In ferromagnets, the degree of magnetic anisotropy is represented by the vector \( \mathbf{K} \), which has units of energy density. \( \mathbf{K} \) represents the energy needed to magnetize a ferromagnet along a particular axis. Since the three components of \( \mathbf{K} \) for an anisotropic ferromagnet are unequal by definition, the magnet is said to have an "easy", "medium", and "hard" axis, with the magnet needing the least energy to magnetize along the easy axis, and the highest energy to align with the hard axis.

The two main sources of magnetic anisotropy are magnetocrystalline anisotropy (microscopic) and shape anisotropy (macroscopic). Magnetocrystalline anisotropy arises from the orbital coupling of atoms inside the crystal. Because the orbital coupling relies on the crystal structure, defects in the crystal lattice may cause the anisotropy to change locally. Shape anisotropy comes from minimizing the magnetostatic energy by reducing the area of magnetic stray fields leaving the ferromagnet. In a wire, the surface area of magnetic stray fields is minimized when the magnetization follows the wire axis.

Domain walls in a wire have a component of the magnetic moment that by necessity is perpendicular to the magnetization of the domains on either side. Since the direction of magnetization is heavily influenced by the magnetic easy axis, it becomes energetically favorable for a domain wall’s
2.3 Domain Wall Generation

Within a nanowire, there are several ways of generating magnetic domains. Domains form naturally when a field equal to or larger than switching field is applied to the ferromagnet. During the reversal process, domains aligning with the field form and expand. This is modeled in two ways: the nucleation model, and the pinning model. In the nucleation model, domains form at the outer layers of the material and expand continuously along the wire. In the pinning model, a domain forms between

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**Figure 2.2**: Domain wall generation in a circular wire where the easy axis matches the wire axis. After saturating a wire with a magnetic field, the magnetic moment aligns with the direction of the wire. The domain wall’s position and orientation is tuned by changing the direction of the applied field. Image from [8].
two strong domain wall pinning sites. The potential well of the pinning location prevents the domain from propagating along the wire. A higher switching field is necessary to overcome the potential barrier. The field needed for reversal is related to the maximum slope of the pinning potential, which is the force needed to overcome the maximum pinning strength:

\[ H_c = \frac{1}{2MA} \left( \frac{dU}{dx} \right)_{\text{max}} . \]  (2.3)

Here, M is the magnetization of the wire and A is the exchange stiffness [10]. The precise form of the domain wall potential U(x) is frequently unknown, but the comparison between different wire geometries of the same material can provide a measure of the relative pinning strengths. For example, magnetoresistance measurements can be done at multiple points along the same nanowire surrounding a pinning location to determine if the wire has strong pinning geometry or not.

When the magnetic easy axis aligns with the wire’s axis, a domain wall is easily generated using a semi-circular wire [11]. After saturating the wire with a magnetic field down the middle, the field is turned off. The magnetic moment of the wire aligns with the wire, resulting in a domain wall (see Fig 2.2). The initial position of the domain wall can be tuned by changing the angle of the saturating magnetic field. In a transverse domain, the orientation (head-to-head or tail-to-tail) of the domain wall can also be controlled with the direction of the field.

In the case of strong magnetocrystalline anisotropy, a domain can be generated using an Oersted field. When the ferromagnet has a reasonably small switching field, a domain can be induced by a current running through a perpendicular metallic wire. (see Fig 2.3) [9]. The Oersted field generated by the current aligns with the ferromagnet. A sufficiently strong current can change the magnetization of the ferromagnet. Since the direc-
tion of the field depends on the direction of the current through the generating wire, it is possible to control the direction of the resulting domain. The effect is local: as the field drops off with roughly a $1/r$ dependence, the applied field quickly falls below the switching threshold away from the generating wire.

With magnetocrystalline anisotropy, it also becomes possible that the wire axis is at an angle to the magnetic easy axis. When there is a large aspect ratio, stripe domains may form. These domains form in parallel to each other, and alternate polarity along the length of the wire (see 4.1). The width of the stripe domains relates to both the width of the wire and the overall aspect ratio. Because the domains are randomly spatially distributed, they do not allow for controlled generation.

### 2.4 Depinning and Critical Current

One of the most attractive features of domain wall manipulation is synchronous movement of consecutive domain walls. When a magnetic field shifts a domain wall, the direction of motion depends on the orientation of the domain: head-to-head versus tail-to-tail domain walls (HH or TT) move in opposite directions under the same field. Since by necessity consecutive domains alternate orientation, a magnetic field cannot move domain walls without changing the shape and size of the domains. Using a current, however, both types of domains move in the direction of the current. When a current moves domain walls, the information about the domain is preserved.

There are two methods of transport for domain walls via current. In thin walls with an abrupt transition between domains, wall transport hap-
pens through momentum transfer of the reflection of conduction electrons off the wall. This momentum transfer is proportional to the current. Thin walls are expected in magnetic nanocontacts (e.g. small particles or grains) with large magnetoresistance.

In thick walls, the primary motivator is spin-transfer, though electron scattering does still happen. In a thick wall, the current polarization follows the magnetic moment of the ferromagnet adiabatically. When the wall is thick, the transition between two domains is gradual. As the electrons cross the domain wall, they exert spin-torque on the magnetic moment. The electrons experience opposite torque that keeps them aligned with the magnetic moment. As the current passes through, the now-shifted electrons interact with the next part of the domain, allowing the domain wall as a whole to shift along the wire.

To move a domain wall, a threshold current is necessary, even when the domain wall is not explicitly pinned. Torque and momentum from the current get absorbed by the magnetic anisotropy, which resists the change in magnetic moment inside the domain wall itself (perpendicular to the easy axis). When there are no pinning sites, the critical current is proportional to the hard-axis magnetic anisotropy [7], and depends on the spin polarization of the current:

\[
I_c = \left(\frac{2e}{h}\right) \left(\frac{\alpha}{P}\right) VM_s (H_K + 2\pi M_s),
\]

where \(\alpha\) is the Gilbert damping parameter, \(P\) is the spin polarization of the current, \(V\) is the volume of the domain, \(M_s\) is the saturation magnetization, and \(H_K\) is the anisotropy field [3, 12, 13]. For applications such as racetrack memory, it is important to shift domain walls reliably between two pinning sites, so the presence (or lack of) a domain wall can accurately be determined for each bit. The average speed of the wall depends on how the relative magnitude of the current to the critical current [7]:

\[
< v > \propto \sqrt{(j/j_c)^2 - 1}
\]

High critical currents bring the danger of rapidly heating, melting, or otherwise damaging the wire. The critical current needed to push a domain out of a pinning potential can be lowered by making use of resonant amplification. With pinning potentials and the ability to be pushed, domain walls behave like particles with mass [8]. Like a mechanical oscillator, domain wall potential wells have a innate precessional frequency. In the presence of a current, the domain wall experiences damped oscillatory
Figure 2.5: Probability of domain wall motion as functions of current pulse amplitude and duration. The probability is calculated by averaging the response of 30 domain walls to the current pulse. When the current opposes the applied field, an oscillatory dependence on the pulse length develops. [11]

motion [1]. If the current is cut off during the oscillation, the domain wall settles into a new equilibrium position, as shown in Fig. 2.4 [11]. When the current is applied in short bursts (pulses), the oscillations can resonate to increase (or decrease) the probability of depinning the domain wall, without needing to change the current amplitude (See Fig. 2.5). Importantly, at an optimum pulse length, a lower current amplitude is needed for depinning the domain wall. Pulse lengths of half integers of the potential well’s precessional frequency ($\frac{1}{2} \tau, \frac{3}{2} \tau, \frac{5}{2} \tau, ...$) increase the probability. These pulse lengths bring the domain wall farthest from equilibrium.

2.5 Chromium Dioxide

A high spin polarization brings about a lower critical current (Eq. 2.4, $I_c \propto 1/P$) and a larger resistance area product. Half-metals are a special type of ferromagnet that display 100% spin polarization. In a half metal, the energy shift of electron bands due to the internal magnetic field is large to the point where only one of the bands is conducting. The Fermi energy level is completely spin-polarized, leading to a current that is also 100% spin polarized [2]. Because of this, a half-metal is a natural choice of material to consider in the development of reliable domain wall pinning technology.

Figure 2.6 shows the density of states for chromium dioxide, a well known half-metallic ferromagnet [14]. The minority spins experience a
band gap of approximately 1.5 eV, with a 0.5 eV difference before the minority band can conduct. Additionally, CrO$_2$ remains a ferromagnet up to 393 K, making it an ideal material for room-temperature measurements and applications [15]. As a ferromagnet, CrO$_2$ displays strong magnetocrystalline anisotropy.

Initial measurements found between a 10% and 25% increase of resistance across a domain wall, depending on the alignment with the easy axis [3]. The largest change in resistance was found when the wire was aligned with the easy axis. The resistance-area product was measured to be $0.65 \times 10^{-13}$ $\Omega$m$^2$ at 77 K, three orders of magnitude larger than conventional ferromagnets like Co or NiFe. The critical current density needed to push a domain wall was estimated to be on the order of $10^8$ A/cm$^2$, unexpectedly large despite the spin polarization of the current. To determine the feasibility of CrO$_2$ for devices that rely on the manipulation of domain walls, these measurements need to be confirmed.

**Figure 2.6:** Band structure of CrO$_2$. The shift in energy bands in a half-metal is so dramatic, a band gap is created for the minority spins. In CrO$_2$, that gap is approximately 1.5 eV. The Fermi energy level sits in the middle of that gap, creating a spin-polarized current. Image from [14].
Chapter 3

Nanowire Fabrication

A control over the geometry of nanostructure can be used to design efficient artificial pinning sited exploiting its shape anisotropy. Crystal imperfections (i.e. grain boundaries) in a nanowire pins the domain walls and makes its dynamic stochastic. However, a single crystalline wire with well-defined geometry is a potential candidate to investigate domain wall dynamics. As was described in Section 2.2, a discontinuity in wire width pins a domain wall via shape anisotropy. Such discontinuities require precise manufacturing techniques to achieve the needed tolerances.

3.1 CVD Growth

Chromium dioxide is a meta-stable material which reduces to the more stable Cr₂O₃ (an antiferromagnetic insulator). This happens on the surface of the material, especially when exposed to ambient conditions (where the lost oxygen can form O₂) or metals that oxidize easily, such as copper. Because of this, CrO₂ cannot be grown via sputtering, as it is not possible to create a sputtering target made of CrO₂. CrO₂ can only be grown via chemical vapor deposition (CVD) between 390 °C and 400 °C. In CVD, CrO₂ is grown on a TiO₂ substrate, which closely matches the crystal structure of CrO₂ and allows for epitaxial growth.

To create CrO₂ nanowires, selective area chemical vapor deposition was used. It can also be achieved by etching a CrO₂ film, but the etching process inevitably degrades the quality of CrO₂ [16] and introduces crystal defects at the wire’s edge. By using an amorphous SiO₂-x mask (which has a zero sticking coefficient with CrO₂ due to lattice mismatch), CrO₂ crystals of high quality can be grown in the desired shape.
Figure 3.1 shows an overview of the process used to create a SiO$_{2-x}$ mask. TiO$_2$ substrates were sputtered with a doped SiO$_{2-x}$ layer, to a thickness in the range from 20 nm to 50 nm. To prepare for electron beam lithography, a triple layer of polymethyl methacrylate (PMMA, 600K molecular weight) resist was spin-coated on the SiO$_{2-x}$ at 4000 RPM. Each layer of PMMA was baked at 180 °C for 90 seconds. A fourth layer of conducting polymer was spin coated on top avoid charging effects of the insulating SiO$_{2-x}$ during imaging. Electron beam lithography was used to define a pattern in the resist, which was developed with MIBK/IPA to create a mask in the PMMA. The underlying SiO$_{2-x}$ was etched via reactive ion etching (RIE) to create well-defined trenches of exposed TiO$_2$. After the remaining resist was cleaned off using organic solvents (acetone, isopropanol), epitaxial CrO$_2$ was grown in the trenches using CVD as described above.

For electron transport measurements of the wires, additional metallic contacts were sputter-deposited on the sample. For that, a PMMA mask was created in the same manner as above. Prior to the e-beam lithography, the sample was carefully aligned using CrO$_2$ markers grown via selective area grown. The sample with developed PMMA had 80 nm of silver sputtered. Lift-off was performed using acetone to create contacts 5 µm wide.

### 3.1.1 Structural Characterization of Nanowires

Both scanning electron microscopy (SEM) and atomic-force microscopy (AFM) were used to extensively image samples after CVD growth to determine the structural quality of a wire.

SEM uses a beam of electrons to excite secondary electrons off the surface of a sample. A SEM can create an image with resolution on the nanometer scale within a few seconds. Lower resolution images can be seen in real-time, making SEM an ideal technique for quickly checking large areas. SEM is included as part of e-beam lithography, to align the
sample and focus the beam on the surface. Since SEM uses electrons, insulating substrates (such as SiO$_2$) can have a build-up of charge. This causes an image artifact, making the substrate appear darker. This artifact is most easily seen after zooming out of an area (as seen in Fig 4.3).

AFM uses the force between the sample and a cantilever with an atomically sharp tip to create an image. In so-called AFM “tapping mode”, a laser is reflected off the end of the cantilever. The force—representing the interaction between the sample and the cantilever—is measured from the frequency of the cantilever’s oscillations. By keeping the cantilever at a fixed height, increases or decreases in force correspond to a height profile of the sample. The resolution of the image depends on the quality of the cantilever. A resolution of around 10 nm is expected for an average tip.

Magnetic Force Microscopy (MFM) is a special case of AFM in which the imaging is performed with a magnetized tip. A diverging magnetic field exerts a force on such a tip, so in addition to the regular scan of height and phase, the tip is able to detect magnetic stray fields going into or coming out of the sample. Since magnetic fields follow closed loops, the stray field lines may be extended to determine the direction of magnetization inside a device itself. Trivially, this occurs at the edges of samples, where any field inside the material must exit. When the sample surface has a height variation, there may be stray fields exiting from the sides of the variation, but an image artifact may also appear with the same properties of a stray field, due to the increased error in the height measurement at edges. To determine stray fields exiting from the center of the sample (as would be the case with a domain wall), it is necessary to confirm with the height profile that the surface of the crystal at the location is smooth.

### 3.2 Design Boundaries

In the previous work [4], CrO$_2$ nanowires were fabricated with widths varying from 100 nm to a micron. Depending the width of the wire, two different types of domain walls can be stabilized: vortex or transverse. Thinner wires (on the order of 200 nm) are needed to create transverse domain walls that require lower current density for depinning. To create a pinning site, shape anisotropy perpendicular to the wire axis was introduced by varying the width of the wire along its length.

To control the width and geometry of the wire, e-beam dose test patterns were used. A pattern mimicking the desired geometry is repeatedly written at different exposures. Figure 3.2b shows a typical dose test. 300 nm thick wires were written with varying gaps widths between paral-
Figure 3.2: (a) E-beam pattern used to create narrow, well-defined constrictions (b) SEM image of CrO2 growth on a dose test. Arrow shows direction of increasing dose. Increasing the e-beam dose shifts the wire development from underdeveloped, incomplete wires to overdeveloped, badly defined wires. The dose needed for proper development differs based on the wire width.

lel wires. At low dose (bottom left), the wire are not fully developed, while at higher doses (right), over-exposure lead to thicker wires than merged into each other. In pinning junctions, a matrix of dose tests was used to test combinations of the doses of the wide and narrow regions of the wire, with a deliberate gap in the pattern between the two regions. The space between the two regions gives a very narrow constriction ideal for domain wall pinning when overdeveloped (See Fig. 3.2a)

### 3.3 SiO$_{2-x}$ Sensitivity

Selective area growth of CrO$_2$ occurs via nucleation of CrO$_2$ crystals at the SiO$_{2-x}$/TiO$_2$ interface and then successive growth [6]. Therefore, the quality of SiO$_{2-x}$ is critical for fabrication of high quality wires; even a slight variation affects the growth quality severely. In the following section
we address the effect of SiO$_{2-x}$ quality on CrO$_2$ growth.

### 3.3.1 Proximity Effect

In electron beam lithography, the proximity effect is an issue that arises during the patterning of the resist. Due to interactions with the resist and the substrate, electrons from the patterning beam may backscatter [17]. This underexposes the resist, causing the pattern to fade. When the pattern has nearby features, the electrons scattering from those areas can act as a secondary exposure for the resist, mitigating the blurring. This is especially true with large pattern features. Depending on the size of the feature, the edges can remain underexposed while the center is properly exposed.

This effect can clearly be seen in Fig. 3.3. A change in SiO$_{2-x}$ doping levels was enough to cause the substrate to interact differently with the electron beam (Figs. 3.3b and 3.3c). In Fig. 3.3a, a large square in the middle (100 $\mu$m across) still has mostly the proper exposure, though the corners are rounded off. The labels “100”, “200”, and “300” each develop according to how nearby and how large other features are. In the case of the “100” label, the only part that developed properly is where the two 0s are close to each other. The label “200” is faded on top and to the right and left, but is affected by backscattered electrons from the 200 nm line dose test sitting underneath it. Meanwhile, the “300” label has both the 200 nm line dose test above it and the 300 nm line dose test underneath, and is only faded to the right and left. Small, isolated lines (bottom right corner) never develop properly, even at high doses.

To compensate for the proximity effect properly, the software running the electron beam has to calculate an adjusted dose for each point in the pattern based on the surrounding geometry [18]. This typically requires fine-tuning configuration parameters for the specific substrate, which is a delicate process at best. To address this issue we adopted a new approach: after the resist is developed, the sample was exposed to an O$_2$ plasma for between 4 and 7 seconds. This removes residual resist in the patterned trenches, exposing the silicon layer before etching. The difference in quality can be seen by comparing Figs. 3.3b and 3.3c.

### 3.3.2 Reactive Ion Etching

When etching the SiO$_{2-x}$ layer via reactive ion etching, the appropriate etching time and gas ratio are affected by the amount of doped oxygen in
Figure 3.3: The proximity effect affects the growth of CrO$_2$, especially on edges and smaller features in a sample. (a) Optical image of proximity effect on a test pattern after growth of CrO$_2$ (white) on SiO$_2$-$x$ (gray). (b) Proximity effect on 100 nm features. (c) CrO$_2$ growth on 300 nm features after using O$_2$ plasma before etching. (b) and (c) use a different source of SiO$_2$-$x$. 
3.3 $\text{SiO}_{2-x}$ Sensitivity

Figure 3.4: SEM image of poor $\text{CrO}_2$ growth due to redeposition of radicals on the sidewalls of the trench during RIE. Instead of the smooth growth as seen in Fig. 3.2b, large, disordered grains form along the side of the pattern. Along the narrow tail of the pattern, these grains are frequently wider than the original trench itself.

the layer. The $\text{SiO}_{2-x}$ is etched with a CF$_4$/O$_2$ plasma. The ratio of CF$_4$ gas to O$_2$ gas greatly affects the quality of the etched trench. Depending on the source of $\text{SiO}_{2-x}$, the optimum amount of oxygen is somewhere between 7% and 30% (CF$_4$:O$_2$ ratio from 30:2.5 to 30:15). The quality of the $\text{SiO}_{2-x}$ trench is adversely affected when the gas ratio is more than a few percent away from the optimum ($\pm$3%).

During the etch, F radicals react with $\text{SiO}_{2-x}$ to erode the bottom layer. The concentration of O$_2$ determines the concentration of F radicals, with the maximum concentration of radicals when the plasma is 30% oxygen. The etched products from the $\text{SiO}_{2-x}$ can be oxidized by O radicals, which forms a nonvolatile layer that gets sputtered over the surface of the trench. This prevents further etching of the walls of the trench, but smooths the trench sidewalls [19], increasing the sidewall quality. When the concentration of oxygen is too high, the presence of O$_2$ may block active etch sites. The effects of low and high oxygen concentration means the maximum etch rate happens somewhere between a 10% and 20% O$_2$ concentration [19, 20].

The quality of the etched sidewall is an important factor for determining the quality of the final $\text{CrO}_2$ growth. A poor-quality sidewall leads
The etch rate depends on the optimized gas ratio needed for RIE. Once the ratio is fixed, the trenches show good agreement between all the various line widths. The etch rate is $20.0 \pm 1.0 \text{ nm/min}$ in this case.

Figure 3.5: The etch rate depends on the optimized gas ratio needed for RIE. Once the ratio is fixed, the trenches show good agreement between all the various line widths. The etch rate is $20.0 \pm 1.0 \text{ nm/min}$ in this case.

to a final growth that has the similar appearance to growth when the resist had a very mild proximity effect: the edges of the CrO$_2$ structures have randomly-oriented crystallites, with small features being more pronouncedly affected, as in Fig. 3.4. As the key factor for the quality of the etch is the amount of oxygen present, the doping of the SiO$_{2-x}$ can affect the etch. To achieve the optimal growth of CrO$_2$, the ratio of the two gases should be calibrated to the specific SiO$_{2-x}$ source.

The other relevant etch parameter that determines the final quality of the CrO$_2$ crystal is the duration of the etch. As the CrO$_2$ does not grow on the amorphous SiO$_{2-x}$, the etch needs to be long enough for all the SiO$_{2-x}$ to be removed from the bottom of the trench. However, etching for too long damages the crystal structure of the underlying TiO$_2$ layer. This results in formation of nonuniform CrO$_2$ structures with randomly oriented grains. Moreover, the growth of the CrO$_2$ will also be much slower than for high-quality crystals, as the initial layer of growth has trouble gaining a foothold at the bottom of the trench. The etch time depends on the thickness of the SiO$_{2-x}$ layer (around 40 nm thick), while the etch rate is determined by the gas ratio used for etching. Etch times typically would be around 150 seconds, with a 5 second window (3% of the total time) before the crystal structure of the TiO$_2$ would begin to be noticeably disrupted.
AFM Characterization

Figure 3.5 shows the depth of the trench in the SiO$_{2-x}$ as a function of time, measured using AFM. The thickness of the SiO$_{2-x}$ layer was 39 nm. Irrespective of width, the etch rate is constant across all features. The rate of etching for this particular source of SiO$_{2-x}$, shown as the slope of the line of best fit, is 20.0 ± 1.0 nm/min. The rate remains the same even after the etch reaches the depth of the TiO$_2$ layer.

Figure 3.6 shows AFM images of CrO$_2$ test patterns grown for 40 minutes on a SiO$_{2-x}$ mask created with different sputtering sources and etching times. The height and quality of the test pattern clearly shows the effect of over-etching and the necessity of adjusting the etch time to the SiO$_{2-x}$ sputtering source. Figures 3.6a to 3.6c use the same SiO$_{2-x}$ mask with trenches etched using 15 second intervals. Each increase in etch time leads to progressively poorer growth. In Fig. 3.6a, etched for 150 seconds, the CrO$_2$ growth is relatively clustered together in the middle of the 5 µm by 15 µm. The final height, although uneven, is clearly above the level of the surface of the surrounding SiO$_{2-x}$ layer. In Fig. 3.6b, etched for 165 seconds, there is still clearly growth, but the CrO$_2$ is comprised of smaller crystals dispersed along the bottom of the trench. In Fig. 3.6c, etched for 180 seconds, there is barely any growth at all. By comparing the AFM images of a trench just before and after the selective area CrO$_2$ growth, it becomes clear that the height differences in CrO$_2$ are not simply due to a difference in trench depth, but that the disrupted crystal structure of the underlying TiO$_2$ causes slower growth under the same CVD conditions.

Figure 3.6d shows a sample with proper crystalline growth of CrO$_2$ that used a different sputtering source of SiO$_{2-x}$. Despite being etched for the same length of time (165 seconds) as the sample in Fig. 3.6b, the quality of the growth is much higher, with faceted CrO$_2$ growth over the whole trench.
Figure 3.6: AFM images show a stark contrast in the growth between (a-c) over-etched samples sharing a common SiO$_{2-x}$ mask and (d) a properly-etched sample using a different sputtering source. In all samples, CVD done for 40 minutes. The color of the image represents height of the sample in nanometers. As the samples get progressively more over-etched, the resulting crystal grains become smaller, shallower, and more dispersed. Note that (a-c) have larger dimensions than (d).
Results and Discussion

There are several categories of measurements that characterize domain walls inside CrO$_2$ nanowires. MFM was used to characterize a domain wall and its pinning at the artificially-created sites (notch, constriction). To probe the dynamics of the domain walls as a result of changing current, field, or temperature, electron transport measurements were performed on CrO$_2$ nanowires. The behavior of the resistance under a changing environment provides an understanding of the structure of domain walls as well as the mechanism of their nucleation and propagation.

4.1 Magnetic Characterization of Domain Walls

To characterize the devices efficiently, the internal magnetic fields of the samples were studied using MFM. In MFM images, light and dark contrast represent magnetic fields pointing up and down, not necessarily respectively. By consistently drawing an arrow from light to dark, it becomes possible to determine the relative direction of the magnetization of the CrO$_2$. Figure 4.1 shows MFM images of a CrO$_2$ test pattern in its virgin state, with the magnetization that occurred spontaneously after growth. In both MFM images (Figs. 4.1a and 4.1d), contrast is observed only on the right and left edges of the growth, indicating that all magnetic domains lie along a single axis. This is due to the strong magnetocrystalline anisotropy of CrO$_2$, dictated by the [001] crystalline direction of the underlying TiO$_2$. Even when the wire axis is perpendicular to this direction, the magnetic field preferentially aligns with it—a sign that in this material, the intrinsic crystalline anisotropy dominates the magnetic behavior. The edges of the larger top and bottom pads in Fig. 4.1a show thin stripe-like domains
Figure 4.1: (a) MFM stray magnetic field measurement. The crystalline [001] direction aligns with the magnetic easy axis. (b) The direction of magnetization inside (a). On this scale, the stray field from the constriction make it impossible to see if any domain walls lie between the two larger side pads. (c) Height profile of (a), shown also in Fig. 3.6d (d) A zoomed-in image of a different part of the sample shows no domain wall, though clear surrounding stray fields. A bump in the middle-left of the image shows faint dark and light stray fields. On both samples, there is a characteristic stripe pattern in the hard axis magnetism, even though the height profile remains uniform.
4.1 Magnetic Characterization of Domain Walls

Figure 4.2: Domain wall (D) created due to the influence of nearby wires. See Appendix A for full image and height profile.

when the wire axis aligns with the magnetic hard axis (See Fig. 4.1b). The size and positioning of these domains are determined by the interplay between magnetocrystalline and shape anisotropy. This strong preference for aligning with the easy axis is the primary reason that the technique for controlled domain wall generation illustrated in Fig. 2.2 would not work for CrO$_2$ structures.

At first, the middle section in Fig. 4.1a appears to be magnetized opposite to the direction of the two side pads, indicating a domain wall. However, strong dark and light contrast can saturate the image. When the image is saturated, contrast blurs into the surrounding area, as seen at the constrictions. In Fig. 4.1a, the resolution of the image makes the presence of a domain wall at the constriction uncertain. By increasing the resolution or spatial separation, the presence of a domain wall can more accurately be confirmed. In Fig. 4.1d, the constriction shows dark contrast, though not enough to be a domain wall, illustrating the false positives that may come about as a result of saturation. To properly confirm the presence of a domain wall, the stray field contrast needs to be clearly seen coming from the center of the structure. The presence of a single domain wall may also be deduced if the far edges of the sample along the easy axis are both the
same color.

It is possible for domain walls to form in a structure’s virgin state. During spontaneous magnetization of a sample, parallel wires in close proximity to each other are affected by the magnetization of their nearest neighbors due to the dipolar interaction. This leads to a natural alternation of the magnetization in neighboring wires, as seen in Fig. 4.2, wires A-C. However, in a row of wires, two wires separated from each other can be the first to magnetize, and thus dictate the magnetization direction for their neighbors. Since these would have a spatial separation, they are not affected by dipole interaction from the other, and thus random magnetized relative to the other. As the rest of the wires magnetize, alternating directions, there is then a 50% probability of a wire in between the initial two wires which has two neighbors that are opposite each other. With such a mismatch, one wire is influenced to magnetize in two directions leading to a DW formation to minimize the magnetostatic energy (see Fig. 4.2 D). Unlike the head-tail-tail or tail-head-head pattern of C and E respectively, showing the stray fields at each end and in the central constriction, D follows a pattern of tail-head-tail, indicating a HH domain wall at the constriction. The presence of a spontaneously-formed domain wall at the constriction indicates that the shape properly acts to pin the domain wall along the wire.

4.2 Magnetoresistance

While MFM characterizes static domain wall pinning, magnetoresistance measurements provide information about domain wall generation and dynamics under the influence of an external drive i.e. temperature, electrical current, and magnetic field etc. After growth of the CrO$_2$ wire, silver contacts were placed on a wire as the inner two probes in a Kelvin (4 probe resistance) configuration, on either side of the constriction constriction (potential pinning site). The voltage probes were naturally high-impedance because of a layer of insulating Cr$_2$O$_3$ that inevitably forms on the surface of the metastable CrO$_2$. A constant current of 10$\mu$A was injected via large CrO$_2$ contact pads. The disruptive nature of wire-bonding on the contact pads served to circumvent the insulating Cr$_2$O$_3$ layer. The devices were measured using a Physical Properties Measurement System (PPMS) that included both a liquid-helium cryostat and a 7 T magnet.

Two devices, shown in Fig. 4.3, were measured in the PPMS. The magnetoresistance was measured at different temperatures and field orientations. When not in thermal equilibrium, a device showed a creep in
4.2 Magnetoresistance

Figure 4.3: SEM images of the devices measured in the PPMS system for magnetoresistance properties. A narrow CrO$_2$ wire is shown between the surrounding metallic voltage probes. In (a), a small constriction in the wire width may act as a pinning site, while in (b), the wire remains a constant width except for a small length of increased width.

average resistance value over time. The change in resistance from this creep was generally large enough to mask the change in the resistance caused by the applied magnetic field. Both devices were allowed to attain thermal equilibrium and were measured simultaneously by first saturating the magnetic field in the negative direction, then sweeping the field to saturation in the positive direction and back. The resistance between the two voltage probes at each point was recorded as a function of applied field and temperature. Figure 4.4 shows a typical magnetoresistance measurement. When normalized, the two samples show the same percentage change in resistance despite being different in their dimensions and having different zero-field resistances. Although the change in resistance is only a small percentage of the mean resistance, between -0.20% and +0.12%, amounting to at most a couple Ohm, the consistency of the measurement suggests that the difference is believable.

In Fig. 4.4, the switching field $H_c$ is taken to be the absolute value of the magnetic field at the two peaks in resistance. For each, the field was first set to a large negative value to saturate the ferromagnet. As the field swept from negative to positive, the resistance was measured at different fields in steps of 100 Oe. Once saturated in the positive direction, the field was swept back to the lower limit to complete the hysteresis loop. The magnetic field at the peak represents the lower bound of the switch-
Results and Discussion

Figure 4.4: Magnetoresistance hysteresis loop at 100K. Blue and green lines represent different samples with $R(0) = 492 \, \Omega$ and $695 \, \Omega$ respectively. Here, the field is applied along the easy axis. Arrows indicate the direction of the field sweep in each section.

Figure 4.4: Magnetoresistance hysteresis loop at 100K. Blue and green lines represent different samples with $R(0) = 492 \, \Omega$ and $695 \, \Omega$ respectively. Here, the field is applied along the easy axis. Arrows indicate the direction of the field sweep in each section.

In all cases, both devices had the same switching field with very little variation. Equation 2.3 implies that this means both devices have equal pinning strength. The likely cause of this is that both devices only have weak pinning because the changes in wire width are not very drastic. However, this may be due to the strong magnetocrystalline anisotropy of CrO$_2$ which dominates shape anisotropy. In that case, even if a constriction, notch, or bulge in the wire is a favorable pinning site (as seen in Fig 4.2), the domain wall may nonetheless be only weakly pinned to the site.

4.2.1 Thermally Activated Magnetization Reversal

To probe the thermally activated DW nucleation and propagation, switching field was measured as a function of temperature. Figure 4.5 shows the temperature dependence of the switching field. For these measurements, the magnetic field was aligned with the wire and magnetic easy axis. The
rise in the switching field at lower temperatures is due to thermally-activated depinning. The temperature-dependence of the activation confirms that domain reversal happens by nucleation and subsequent propagation of the domain walls [21].

If the depth of the pinning energy barrier is controlled by an “effective shape anisotropy” [22], the switching field is expressed as

\[ H_c = H_{c0} \frac{M_s(T)}{M_{s0}} \left[ 1 - \frac{25k_B TM_{s0}^2}{E_0 M_s^2(T)} \right]^{1/m}, \] (4.1)

where \( M_s(T)/M_{s0} \) is the saturation magnetization of the sample (a function of temperature), \( H_{c0} \) is the switching field at 0 K, \( E_0 \) is the barrier height at zero field, and \( m \) depends on the symmetry of the barrier. In this model, \( H_{c0}, E_0, \) and \( m \) are fitting parameters. With an unknown form of \( M_s(T) \) (which on the shape of the wire, here a mix between thin film and grains), it is impossible to tell if the data would fit this form. Additionally, with 3 parameters to fit to only 5 points, almost any form of equation would fit artificially, within a margin of error. However, considering the strong magnetocrystalline anisotropy and the consistent switching field between the two samples, it is doubtful that the shape anisotropy plays a large role in this case.
4.2.2 Magnetization Reversal Mode

Angular dependence of switching field can provide understanding of domain wall structure as well as magnetization reversal mode in a magnetic structure. Figure 4.6 show the switching field of the devices as a function of the angle of the applied magnetic field while at a constant temperature. The field was swept from aligning with the easy axis (in-plane) at 0° to pointing out-of-plane at 90°. As the angle increases, so does the switching field, until a peak is reached at 90°. Past 90°, the field starts to lie in-plane again (fully in plane at 180°). Since the measurement is symmetric with regard to the direction of the magnetic field, measuring at ±θ should give the same value for the switching field. As seen in Fig. 4.6, the switching field is symmetrical around both 0° and 90°. The quadrant repeats such that measuring the full 360° would give a second peak at 270° and a second minimum at 180°.

In a nanowire in the weak pinning limit, there are two modes of reversal considered important: coherent rotation and curling rotation [23]. In coherent rotation, the magnetic moments change while keeping a uniform orientation. This is indicative of a transverse domain wall. The energy of the coherent rotation mode has a term added because of the Zeeman
4.2 Magnetoresistance

Effect [24], leading to a switching field that follows

\[ H_c \propto \left( \cos^{2/3}(\theta) + \sin^{2/3}(\theta) \right)^{-3/2}. \]  \hspace{1cm} (4.2)

This equation describes a switching field whose magnitude decreases from 0° until it reaches a minimum at 45°, before increasing again [6].

In curling rotation, reversal happens via the propagation of a vortex domain wall. Because the domain wall is spatially symmetrical, the Zeeman term is negated. This leads to a switching field of the form

\[ H_c \propto \frac{a(a+1)}{\sqrt{a^2 + (1 + 2a\cos^2(\theta))}}. \]  \hspace{1cm} (4.3)

where \( a \) is a factor relating the wire diameter to the exchange length [23]. In this case, the function monotonically increases until 90°, where it reaches a peak. Although this form applies specifically to infinitely long cylindrical wires, it is sufficiently different from the form for the switching field of coherent rotation to permit differentiation of the type of reversal observed. Figure 4.6 clearly shows a monotonic increase. The nanowires shown in Fig. 4.3 are wide enough to accommodate vortex domain walls, and the magnetization reverses via curling rotation.
Conclusion and Outlook

In this report, we have studied several synthetic parameters which critically determine the quality of CrO$_2$ nanowires. Using magnetic force microscopy, we have shown that the domain state in CrO$_2$ nanowires are determined by the interplay magnetocrystalline and shape anisotropies. This results in homogeneous magnetization along the magnetic easy axis in an isolated nanowire, and stripe domains along the magnetic hard axis. In CrO$_2$, the magnetic anisotropy is dominated by the magnetocrystalline anisotropy, so the easy axis aligns with the crystalline [001] axis. The strong temperature dependence of the switching field indicates the domain wall nucleation and propagation, resulting in reversal of the magnetization, is thermally-activated. This also suggests that the effect of shape anisotropy on the reversal process is negligible.

Magnetoresistance measurements showed that two nanowire devices of different dimensions had the same switching field, implying that neither had strong pinning. We observe that the switching field shows an angle dependence characteristic of curling reversal mode. This implies the presence of vortex domain walls, which is expected for CrO$_2$ nanowires wider than 500 nm. In the weak pinning limit, the switching field for CrO$_2$ ranged from 500 Oe up to 2000 Oe, depending on the relative field orientation to the easy axis. The large switching field and magnetocrystalline anisotropy mean that the methods described in Ch. 2 to generate domain walls [9, 11] would not work for CrO$_2$ nanowires.

It may be possible to determine the depth of a pinning potential geometry by comparing different sections along the same nanowire. Since the switching field is proportional to the depinning force in the strong pinning limit, MR measurements of a pinning location should show an increase in the switching field compared to a smooth portion of the wire. This would
allow different pinning geometries to be compared to a baseline, allowing for better design of the wire. An increased potential depth would allow for more tolerant RM devices, with less risk of overshooting a successive pinning location when the domain wall is in motion. A domain wall potential well could be further characterized by using current pulses to determine a parabolic processional frequency. This would also serve to reduce the critical current.

In order for CrO$_2$ to be used in RM memory, further investigation into the domain wall pinning mechanisms and critical current density is needed. Wide wires give rise to vortex domain walls, which require a higher critical current density than transverse domain walls. The ability to make narrow nanowires is limited by the reliability of device fabrication process: for crystalline CrO$_2$ nanowires, a reliable sputtering source of SiO$_{2-x}$ is essential.
Appendix A

Full Image of MFM Domain Walls

Figure A.1: Full image of Fig 4.2 without arrows.
Figure A.2: Height profile of Fig 4.2.
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