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Application of Gettering Layers for Low Temperature Conversion of Magnetic Oxides into Ferromagnetic Metals in Thin Films, Multilayers, and Nanostructured Arrays

A Dissertation

Presented to

the Faculty of the Materials Science and Engineering Program

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in Materials Science and Engineering

by

Wenlan Qiu

August 2015

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Abstract

Nanoscale patterning of magnetic metals and their alloys remains a significant challenge due to the lack of reactive-ion etching (RIE) chemistries producing volatile compounds of magnetic elements. Patterning is typically achieved either via a pre-etched substrate deposition, lift-off process, ion milling, or wet etching, all lacking the needed fidelity to achieve the high resolution and high areal density because of fabrication issues such as fencing, shadowing, edge damage, redeposition, or magnetic material residual. Alternatively, electrochemical deposition may circumvent these fabrication issues and produce high aspect ratio structures, but is difficult to make complex structures, i.e., Co/Pd or Co/Pt multilayers, and CoCrPtX alloys, which are widely studied to be the potential candidates for magnetic recording media with areal density beyond 1 Tb/in².

This work demonstrates conversion of nonmagnetic cobalt oxide (CoO) into ferromagnetic cobalt (Co) in thin films, multilayers, and nanostructured arrays by low temperature annealing in the presence of tantalum (Ta) gettering layers. Thin film of CoO sandwiched between Ta seed and capping layers can be effectively reduced to a magnetic Co thin film by annealing at 200 °C, whereas CoO does not exhibit ferromagnetic properties at room temperature and is stable at up to ~ 400 °C. The CoO reduction is attributed to the thermodynamically driven gettering of oxygen by Ta, similar to the exothermic reduction-oxidation reaction observed in thermite systems. Likewise, annealing at 200 °C of a nonmagnetic CoO/Pd multilayer results in the conversion into a magnetic Co/Pd multilayer with perpendicular anisotropy. A nanopatterning approach is introduced where CoO/Pd multilayer is locally reduced into Co/Pd multilayer to achieve magnetic nanostructured array in the presence of Ta islands. Magnetic properties of thin films, multilayers, and patterned arrays in this work are measured on

MicroMag alternating gradient force magnetometer and self-built polar magneto-optical Kerr effect magnetometer. A Physical Electronics 5700 X-ray photoelectron spectroscopy is used to characterize the chemical states and compositions. This technique can potentially be adapted to nanoscale patterning of other systems for which thermodynamically favorable combination of oxide and gettering layers can be identified.

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CHAPTER 1 BACKGROUND AND REVIEW

1.1 Getter Materials

1.1.1 What is Getter?

Getters are a class of reactive materials that is often placed inside a vacuum deliberately to improve the efficiency of that vacuum by scavenging unwanted contaminants. Essentially, gaseous impurities can be removed when striking the getter material, by strong and rapid reaction both chemically and physically. Historically, the first getter materials were thin barium and titanium coatings deposited on glass walls of electronic lamps in order to absorb nitrogen and oxygen traces [1].

Over the past decades, getters are used extensively in getter sputtering to improve film purity by reducing reactive gas components in the substrate deposition zone [2, 3, 4]. Fig. 1.1 presents a simple getter sputtering system, where two cathodes of the material, getter and target, are located symmetrically in a protective cylinder. When the gases enter the bottom of the cylinder, the maximum gettering action occurs at the lower cathode. After sputtering for a few minutes, when all the reactive gases have been gettered, the shutter is removed and the material from the higher cathode is allowed to deposit on the substrates [5].

1.1.2 Getter Properties

The action of a getter material depends on:

- Adsorption (i.e., accumulation of gas molecules at the surface);
- Absorption (i.e., diffusion of gas molecules in the solid);

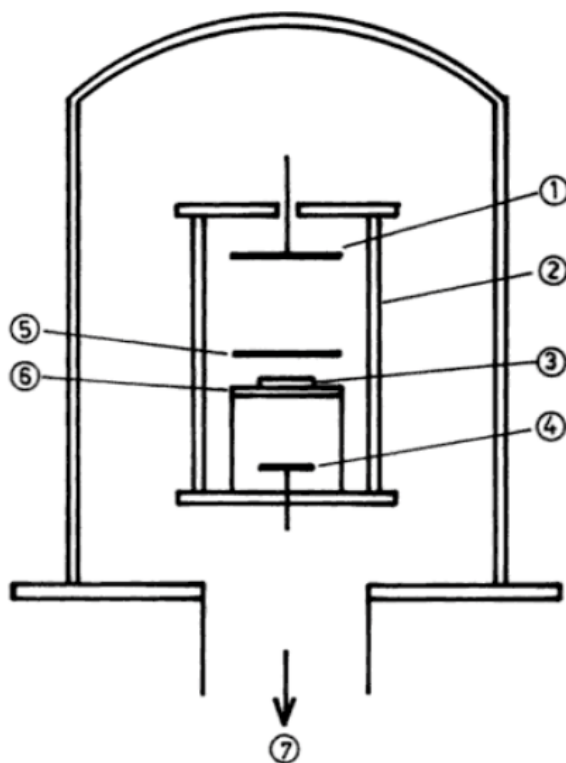


Figure 1.1: Schematic diagram of a simple getter sputtering system: 1) cathode; 2) protective cylinder; 3) substrate; 4) auxiliary cathode; 5) shutter; 6) anode; 7) pump.

Table 1.1: Typical Getters

Gaseous Impurities	Typical Getter Material	Type
Oxygen	Ba, Ti, Zr, Hf, V, Nb, Ta	Permanent
Nitrogen	Ti, Zr, Hf, V, Nb, Ta, Eu, Y, Th, U, Ce	Permanent
Hydrogen	Ti, ZrVFe	Reversible
Water	Ba, Na, K, Li, Cs, Rb	Permanent
Carbon dioxide	Li, KOH	Permanent
Carbon monoxide	Cupric salts	permanent

- Chemical binding (i.e., reaction with the surface atoms).

In addition, it is also important to distinguish getters based on the impurities they remove and the reaction is permanent or reversible. A list of typical getter materials and their properties are presented in Table 1.1.

1.1.3 Tantalum as a Getter Material

Researches and experience have showed that tantalum is a classical example of getter material that plays a predominant role in vacuum systems [2, 6, 7, 8]. Similar to titanium, tantalum as an oxygen getter, is sputter evaporated on the vacuum bell jar walls prior to subsequent metals to reduce oxygen contamination during metallization structuring [9]. Starting from 350 °C, pure tantalum is capable of absorbing gases in amounts up to several hundred times its own volume, and the optimum gettering temperature appears to be around 1000 °C [10]. The main disadvantages of using tantalum as getters are the high material cost and high temperature range required for proper degassing and subsequent gettering operation.

1.2 Oxygen Diffusion in Solid State Materials

Diffusion in solids remains an important topic of metallurgy and materials science, which plays a key role in the kinetics of many micro- and nano- scale changes during processing of metals, alloys, ceramics, semiconductors, glasses, and polymers. The mechanisms of diffusion in atomic level are closely connected with defects. The very simple example can be point defects such as vacancies or interstitials. Dislocations, grain boundaries, phase boundaries, and free surfaces are other types of defects in crystalline solids, all of which can act as diffusion short circuits since the mobility of atoms along such defects is usually much higher than in the lattice. In crystal solid state, diffusion occurs either by interstitial or substitutional (vacancy) mechanisms. In interstitial lattice diffusion, a diffusant will diffuse in between the lattice structure of another crystalline element. In substitutional lattice diffusion, self-diffusion for example, the atom can only move by substituting place with another atom, which is often contingent

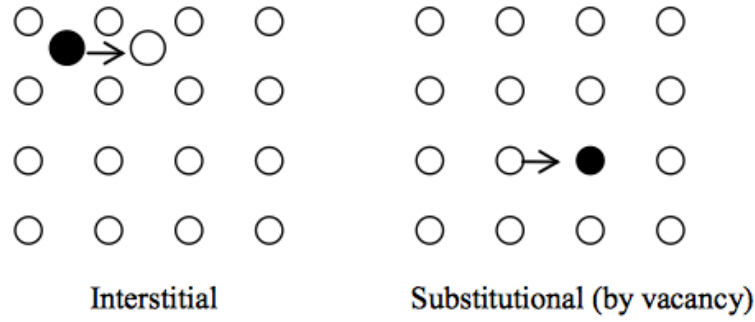


Figure 1.2: Interstitial diffusion and substitutional diffusion

upon the availability of point vacancies in the crystal lattice. Fig. 1.2 illustrates the difference of these two types of diffusion mechanism.

1.2.1 Diffusion Coefficient and Diffusion Equation

Diffusion describes the spread of particles through random motion from regions of higher concentration to regions of lower concentration, which is related to the mass transfer driven by a concentration gradient. The time dependence of the statistical distribution in space is given by the diffusion equation.

The diffusion atoms through a solid can be described by Fick's equation that relates the diffusion flux to the gradient of the concentration via

$$J = -D\nabla C, \quad (1.1)$$

where J is the diffusion flux, D is diffusion coefficient tensor, and C is the concentration. Diffusion coefficient D depends on a couple of environment parameters such as temperature, crystal structure, pressure, etc, and needs to be modified for different types of diffusion activities. Nevertheless, we can still describe a general approximation for diffusion time by

$$t \approx \frac{x^2}{2D}, \quad (1.2)$$

where x is the mean distance traveled by the diffusant in one direction after elapsed time t .

1.2.2 Experimental Methods

Methods to measure diffusion coefficients can be grouped into two major categories: direct methods that are based on Fick's laws and indirect methods that requires a microscopic model of jump process and uses the Einstein-Smoluchowski relation to deduce a diffusion coefficient.

Tracer method is the most direct and most accurate technique for the determination of diffusion coefficients in solids. A radioactive isotope of the investigated atomic species is normally used as tracer, which is deposited on to a polished, flat surface of the diffusion sample. An isothermal diffusion anneal is performed at some certain temperature for some diffusion time and the concentration-depth profile is observed by a serial sectioning of the sample. Sputter sectioning techniques is used for diffusion studies at low temperature, which makes diffusion lengths resolution in the micrometer or nanometer range possible. Other profiling and detection methods include Secondary Ion Mass Spectrometry (SIMS), Electron Microprobe Analysis (EMPA), Auger Electron Spectroscopy (AES), Rutherford Backscattering Spectrometry (RBS), Nuclear Reaction Analysis (NRA), Field Gradient Nuclear Magnetic Resonance, and so on.

Indirect methods measure quantities like relaxation times, relaxation rates or linewidths, and the diffusion coefficient is deduced via the Einstein-Smoluchowski relation,

$$D = \frac{1}{6t} \langle R^2 \rangle, \quad (1.3)$$

where $\langle R^2 \rangle$ denotes the mean square displacement of particles.

1.2.3 Oxygen Diffusion in Metals

The diffusion activity of oxygen diffusion in metals is really slow at room temperature, and the diffusion coefficients are in the range of 10^{-10} to $10^{-25} \text{ m}^2\text{s}^{-1}$ as temperature increases [11, 12, 13, 14]. The diffusion activity highly depends on the crystal structure of the metal and the pressure as well.

1.3 Magnetic Anisotropy and Co/Pd multilayer

1.3.1 Magnetic Anisotropy

In magnetic materials, the origin of the spontaneous magnetization is the exchange interaction between spins. This interaction is essentially isotropic, meaning the spontaneous magnetization can point in any direction without changing the internal energy, if no additional interaction exists. However, in actually magnetic materials, the spontaneous magnetization has an easy axis, or several easy axes, along which the magnetization prefers to lie. Rotating away from the easy axis is possible only by applying an external magnetic field. This direction-dependent phenomenon of magnetization is called magnetic anisotropy. Several kinds of anisotropy will be briefly discussed.

Magnetocrystalline anisotropy

Magnetocrystalline anisotropy is intrinsic to the material. It arises mostly from spin-orbit coupling and is related to the crystal structure of the lattice. For example, hexagonal cobalt exhibits uniaxial anisotropy with the stable direction of spontaneous magnetization, or easy axis, parallel to the c -axis of the crystal at room temperature, as shown in Fig. 1.3 [15]. However, for cubic crystals such as iron and nickel, there are more than one easy axis due to its high order of symmetry. At room temperature, the easy axis for iron, which has a body-centered cubic

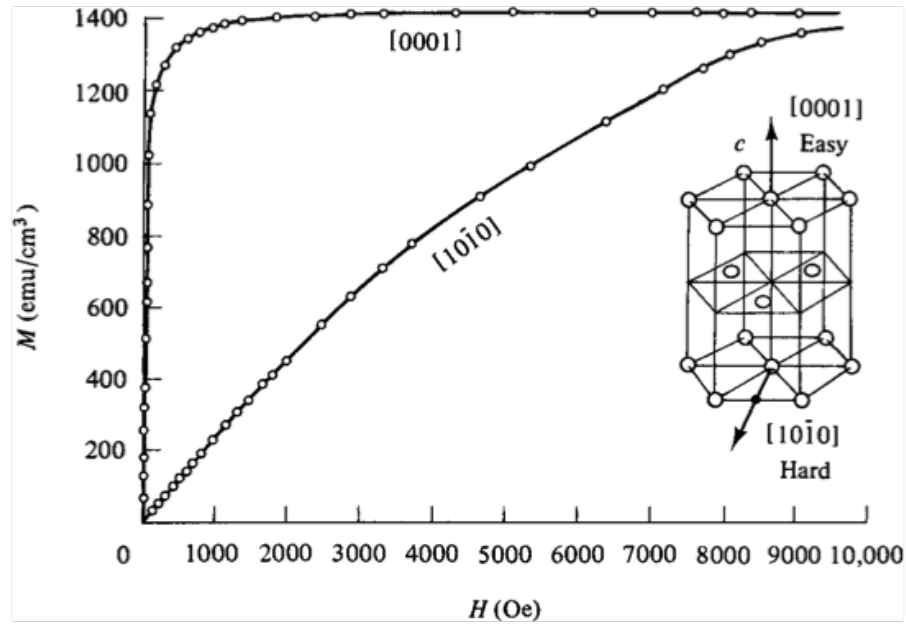


Figure 1.3: Magnetization curves for a single crystal of cobalt

structure, is $[100]$, $[010]$, and $[001]$, and for nickel (face-center cubic), is $[111]$, and its equivalent axes, as seen in Fig. 1.4 [15].

Shape Anisotropy

To understand the shape anisotropy of a material, we need to discuss the internal demagnetizing field first, which is the field within the magnetic material and having the opposite direction of the magnetic field outside of the material. The external field is identical to a field produced by a set of free poles distributed over the surface of the crystal. The surface poles produce the external field, as well as an internal field. The magnetic dipolar interaction is long range and is dependent upon the shape of the sample. Hence shape anisotropy is fairly important in thin film and often produces inplane easy axes.

Consider a polycrystalline material with no net crystal anisotropy. It will be magnetized to the same extent in any direction, if it is a spherical shape. However,

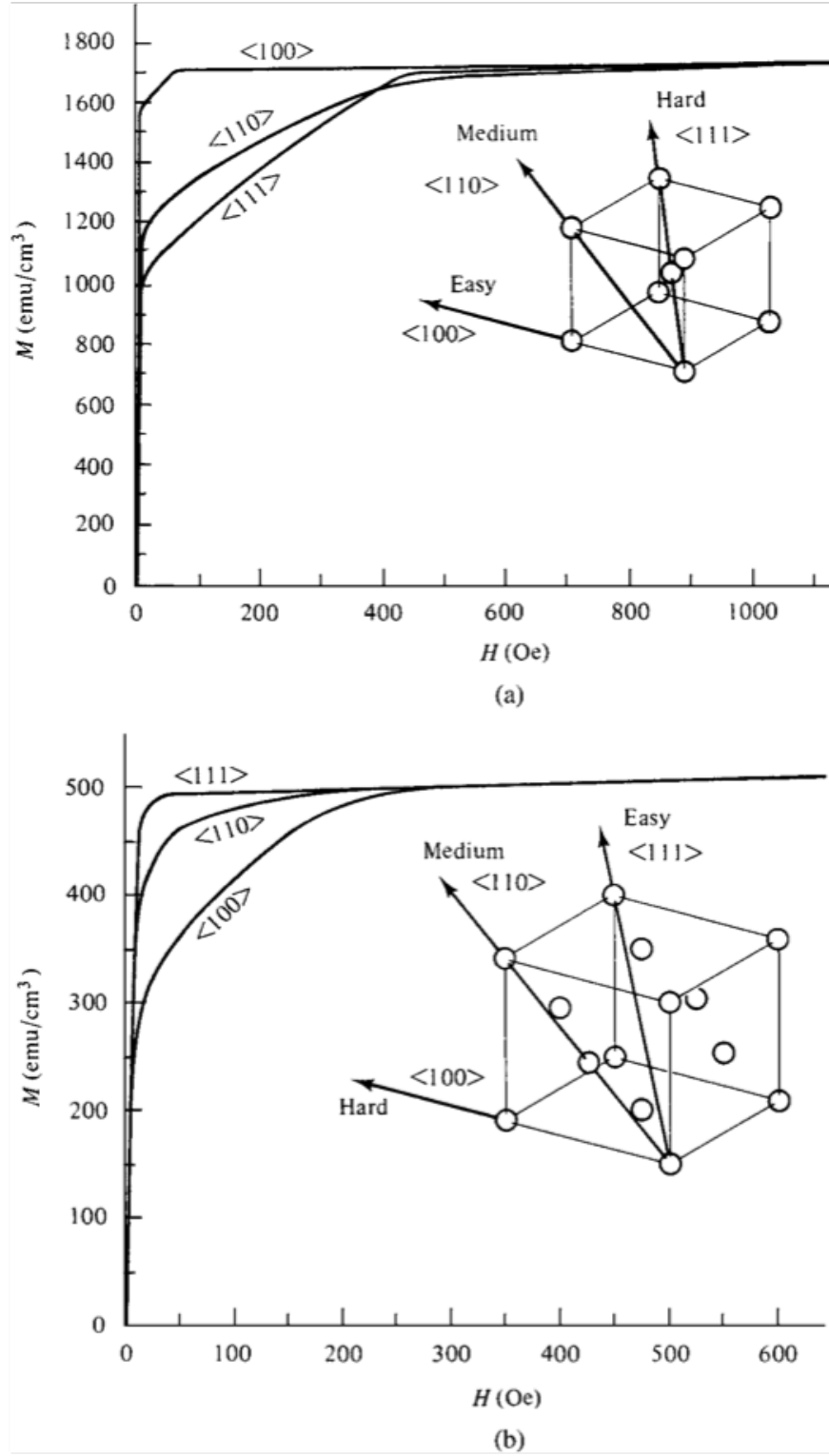


Figure 1.4: Magnetization curves for single crystals of iron (a) and nickel (b)

if it is not, it will be easier to magnetize along a long axis than along a short axis. This is because the demagnetizing field along a short axis is stronger than along a long axis. This shape dependence is the source of shape anisotropy.

Stress Anisotropy

Mechanical stress in materials can be due to lattice misfit, crystalline coalescence, surface stress changes, and magnetization processes, to name just a few. Exchange energy depends strongly on the physical interaction between neighboring atoms, hence stress in the material will affect that interaction. In other words, straining a crystal will alter its magnetic behavior. Similarly, the inverse affect, or the change of dimension of the crystal due to the change in the magnetization can occur. This phenomenon is called magnetostriction and is the source of stress anisotropy.

Exchange Anisotropy

Exchange anisotropy occurs in bilayers or multilayers of magnetic materials where antiferromagnetic and ferromagnetic materials interact. This effect was first observed by Meiklejohn and Bean in 1956 [16], when the hysteresis loop of CoO covered Co is asymmetrical and shifted to the left, after cooling in a strong field to 77 K. Fig 1.5 displays this phenomenon. The physics behind this phenomenon is the exchange interaction between the antiferromagnetic and ferromagnetic at their interface. Unlike the ferromagnetic materials, antiferromagnetics have almost zero net magnetization, their spin orientation is not strongly affected by the external magnetic field. When a soft ferromagnetic film is strongly coupled to the antiferromagnetic layer, the interfacial spins are pinned. Therefore, more energy or field is needed to reverse the magnetization in the ferromagnetic layer, which results in a shift in the switching field. This exchange bias phe-

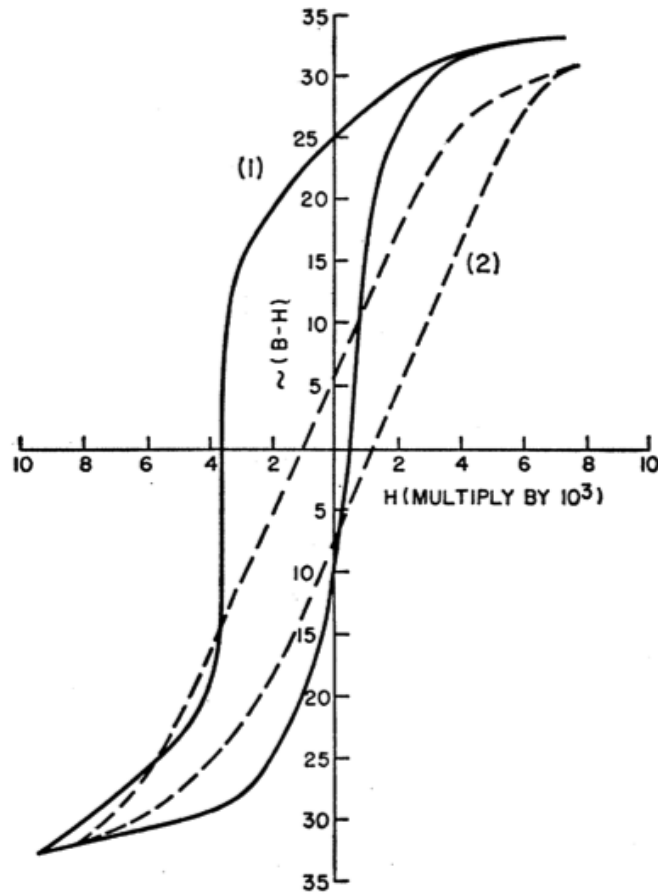


Figure 1.5: Hysteresis loops at 77 K of oxide-coated cobalt particles. Solid line curve results from cooling the material in a 10K Oe field. The dashed line curve shows the loop when cooled in zero field.

nomenon is extremely useful in magnetic recording, where the state of readback heads of hard disk drives at their point of maximum sensitivity is pinned.

1.3.2 Co/Pd Multilayer

Cobalt (Co) is a ferromagnetic material with easy axis in c -axis in its hexagonal close-packed (HCP) crystal structure. Palladium (Pd), on the other hand, is a paramagnetic material, meaning the magnetic moment of the unpaired electrons can point to any direction until an external magnetic field is applied. It is very different from ferromagnetic materials that have a net magnetic moment

with no external magnetic field. As is explained in 1.2.1, thin films tend to have an in-plane magnetic anisotropy due to the strong shape influence. This is true when we make a thin film of Co. However, Co/Pd multilayers, when thickness of each layer carefully controlled, can exhibit perpendicular magnetic anisotropy. This phenomenon has been extensively studied due to Co/Pd multilayers being a promising candidate for high density magnetic recording and next generation magneto-optical recording medium [17, 18, 19, 20].

One of the intriguing factors of magnetic multilayers is the reduced symmetry at the interface, which can result in a considerable contribution to the total anisotropy. In Co/Pd multilayers, the interface anisotropy leads to a preferred direction of magnetization perpendicular to the film plane, when Co thickness is carefully kept below 8 Å [17]. Studies have showed that this perpendicular anisotropy is a result of the competition between an in-plane volume shape anisotropy and perpendicular anisotropy due to the magnetostriction of Co-Pd interface [20, 21, 22]. It has also been determined that the anisotropy is independent of Pd thickness, and the Co thickness needs to be very thin to have a strong perpendicular anisotropy, since Co atoms adjacent to Pd atoms at the interface could induce larger magnetostriction than that of pure Co [20].

1.4 Nanoscale Patterning of Magnetic Thin Films

Patterned magnetic media has been comprehensively studied due to the possibility to circumvent the well-known *magnetic recording trilemma* and provide thermally stable data recording at $> 1\text{Tb/in}^2$. Instead of recording bits on random grains, patterned media provides a well-ordered array of isolated magnetic islands, each of which stores 1 bit. Fabrication of the patterned media is considered the greatest challenge for its commercialization. Therefore, a couple of

patterning schemes have been developed.

1.4.1 Magnetic Recording Trilemma

In magnetic recording industry, the competing and compromising of stability, writability, and readability is commonly known as the *trilemma*. When a higher areal density, the number of bits/unit area on a disk surface, is pursued, a smaller grain volume is preferred naturally. However, the thermal stability is affected with a smaller grain. The energy barrier for magnetization reversal in the presence of an external magnetic field H is given by

$$E_B(H, V) = KV(1 - \frac{H}{H_0})^n, \quad (1.4)$$

where K is the magnetic anisotropy density and H_0 is the intrinsic switching field. The exponent n is 1.5 to account for the 2D random anisotropy axis distribution in isotropic longitudinal media [23]. When finite temperatures are considered, the energy barrier needs to be compared to the thermal activation energy $k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature. Thermally-assisted switching refers to the crossing of an energy maximum with the help of the available thermal energy, and is characterized by a time constant τ [24]:

$$\tau = f_0 \exp(-E_B/k_B T), \quad (1.5)$$

where the attempt frequency that depends on field and temperature is negligible compared to that of the exponential factor. From equations 1.4 and 1.5, it is clear that a reduced grain volume leads to a smaller time constant that can lead to signal decay and potential data loss as the medium is thermally demagnetized.

In the case of this thermal effect, there are a couple of methods with increase in K which counters the reduction in V , can be implemented to improve the thermal stability, such as improving epitaxy, reducing crystallographic defects, and

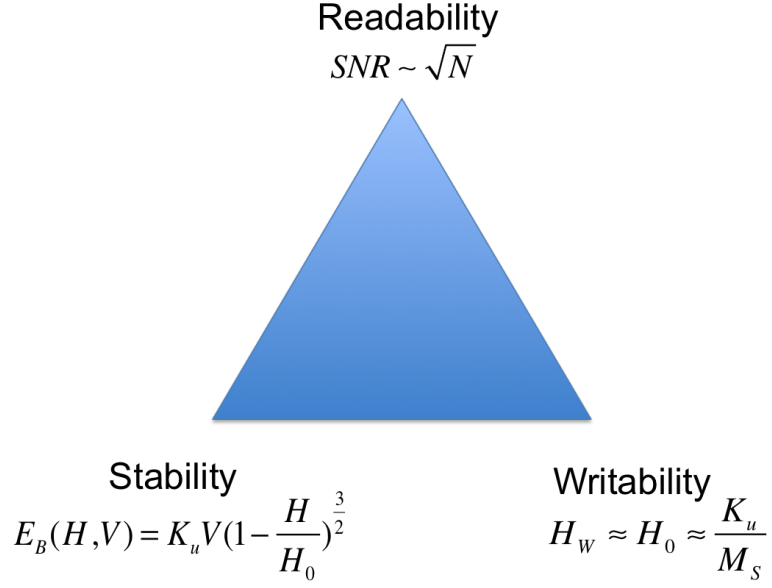


Figure 1.6: Magnetic recording trilemma

using higher anisotropy materials. The latter is currently achieved by increasing the Pt content in modern CoPtCrB media, using tetragonal L1₀ phase FePt and CoPt, or adapting multilayered structures. Nevertheless, following along this path also increases the required write field, since the write field

$$H_w \approx H_0 \approx \frac{K}{M_s}, \quad (1.6)$$

where M_s is the magnetization of the recording media. Unfortunately, the current write poles have already been optimized to produce the highest field value by using low-anisotropy, high saturation magnetization materials.

On the third side of the trilemma is to increase the areal density by having less amount of grains for each bit, which affects the signal-to-noise ratio (SNR) because the SNR is proportional to the square root of the number of grains per bit, from simple statistical estimation [25].

Taking all the factors into consideration, it is increasingly important to avoid limitations of areal growth rates arising from thermal instabilities and significant improvements of the recording medium must be achieved. A number of

innovations has been developed to delay or overcome these limits, including bit-patterned magnetic recording (BPMR), which achieves high SNR and thermal stability by replacing the random grains of conventional media with lithographically patterned magnetic islands that are bigger, and therefore more thermally stable.

1.4.2 Prepatterned Substrates

The initial approach to pattern magnetic thin films was to deposit Co/Pt and Co/Pd multilayers on prepatterned substrates, as illustrated in Fig. 1.7. The multilayers were chosen because their perpendicular anisotropy obtained from interfaces does not rely on crystal anisotropy as much as other well-known high anisotropy systems, such as CoCrPt alloys and $L1_0$ -ordered FePt compounds [26]. This pre patterning approach allows the pillars and trenches to be etched into substrate or under layer materials favorable for reactive ion etching (RIE) and avoids the possible damage to the magnetic layer itself.

The disadvantages, however, include the influence of magnetic property by the material in the trenches and difficulties to adapt this approach for magnetic materials other than multilayers [26, 27]. Fig. 1.8 shows a cross-sectional TEM view of Pt 20 nm/[Co(0.5 nm)/Pt(0.8 nm)]₄ dots prepared by pre patterning technique with 220 nm high, 75 nm wide structure [27]. A rough coating of Co, Pt, and CoPt alloy grains is observed on the sidewalls, and is magnetic at room temperature which induces unwanted ferromagnetic coupling between adjacent dots via deposited material on sidewalls and in the bottom of the trenches [28].

1.4.3 Etching Continuous Films

As lithographic and patterning techniques developed, another way to pattern magnetic thin films is widely used. Fig. 1.9 shows the key steps in the this



Figure 1.7: Prepatterned substrate for patterning magnetic thin films

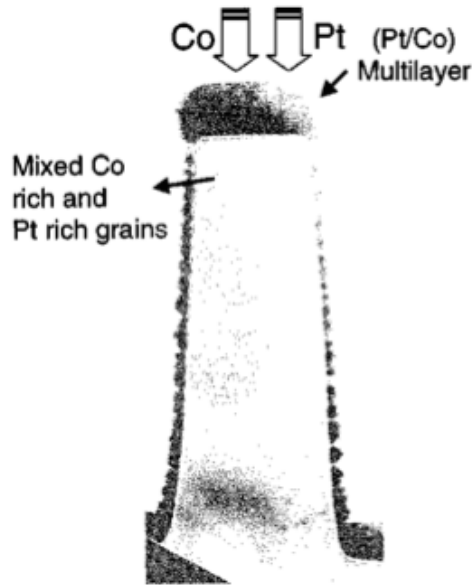


Figure 1.8: Cross-sectional TEM view of Co/Pt multilayer dots using prepatterned silicon substrate

process. First, continuous seed layer and magnetic layer are deposited, on top of which, a certain resist is coated. Electron-beam lithography is used to pattern the resist, followed by ion milling to transfer the structures from the resist layer to the magnetic layer. Finally, the resist is removed and the magnetic layer is patterned to have the same structure as the printed resist. This technique expanded the variety of magnetic materials that could be used, including CoCrPt alloys, which have been studied extensively and currently appear in conventional perpendicular magnetic recording media [26]. Unfortunately, this deposit-then-pattern approach introduces edge damage by ion milling, as seen in Fig. 1.9(F), which is responsible for a low anisotropy for sub-50 nm structures [29].

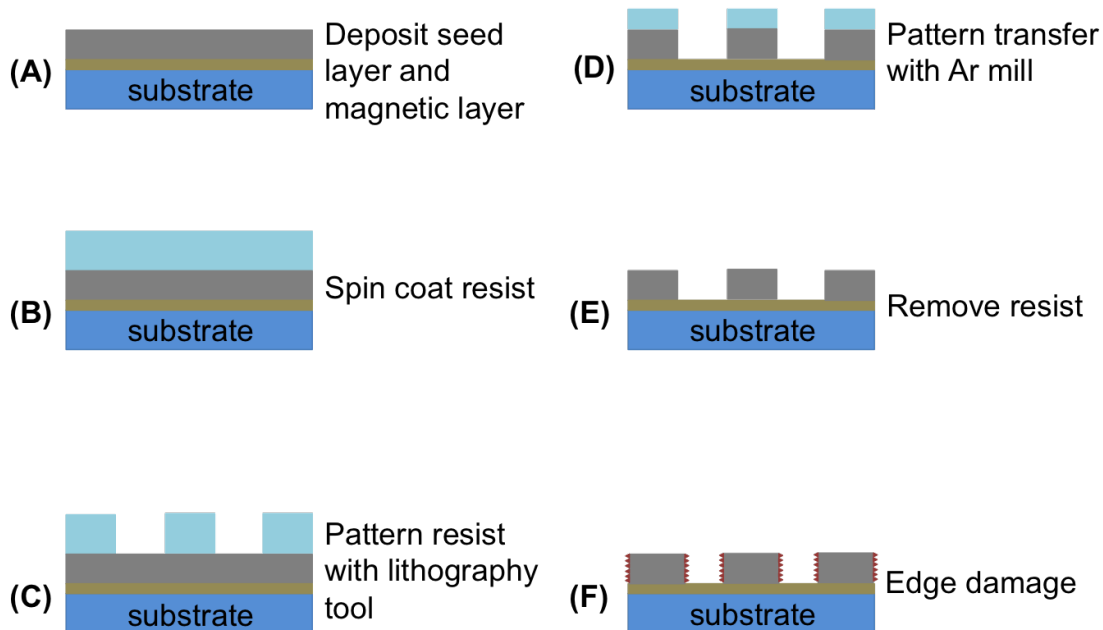


Figure 1.9: Process of patterning magnetic thin films by etching continuous films

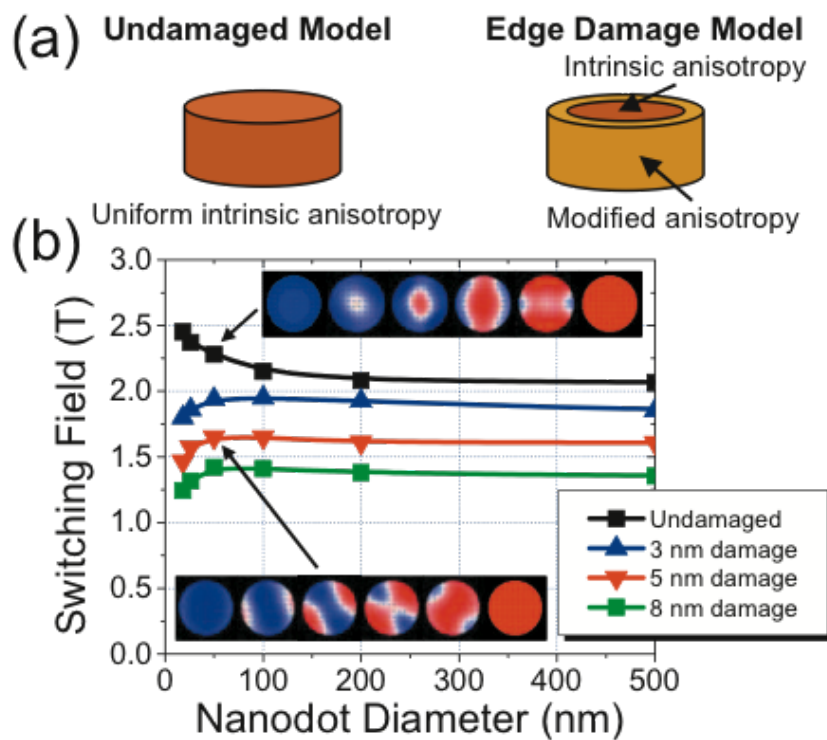


Figure 1.10: Influence of edge damage on switching field properties

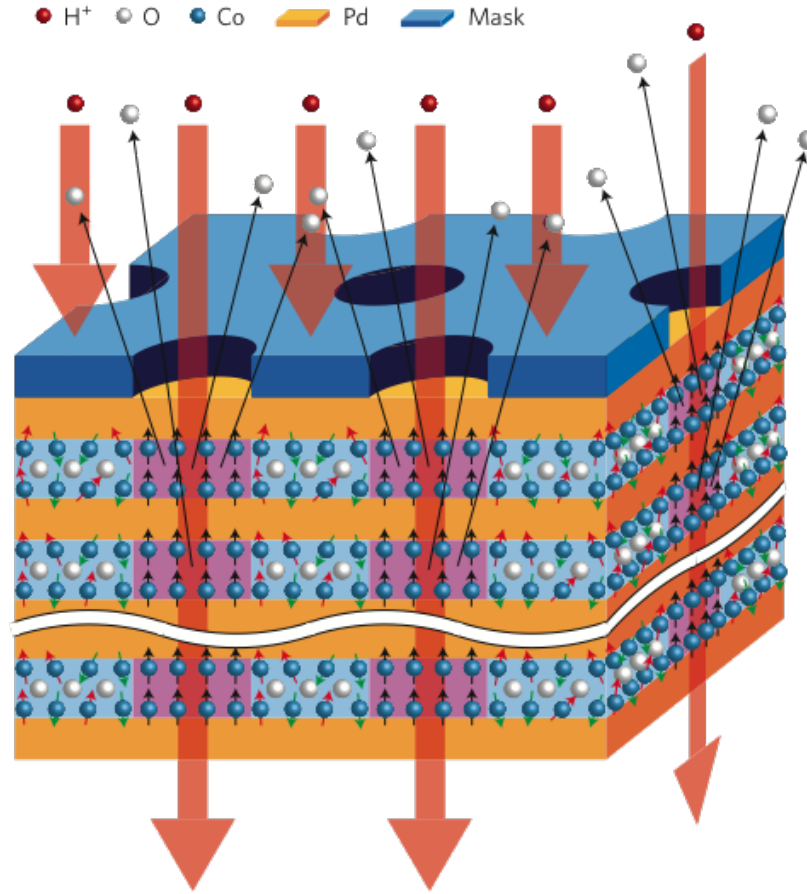


Figure 1.11: Schematic diagram showing proton irradiation converting $\text{Co}_3\text{O}_4/\text{Pd}$ to Co/Pd superlattice

Fig. 1.10 shows the influence of edge damage on the switching field properties of $[\text{Co}/\text{Pd}]_8$ [29]. In uniform anisotropy model, reversal is nucleated in the center or interior of the nanodots, since the edges are stiffer due to the additional energy from magnetostatic edge charges. On the other hand, with only a few nanometers of edge damage, the nanodots express edge nucleated reversal, resulting in a significantly lower switching field as showed in Fig. 1.10(b).

1.4.4 Ion Irradiation

Recently research has revealed the possibility to make nanoscale magnetic structures by reducing magnetic oxides with low-energy proton irradiation [30].

As seen in Fig. 1.11, $[\text{Co}_3\text{O}_4/\text{Pd}]_{10}$, a paramagnetic oxide, is reduced to $[\text{Co}/\text{Pd}]_{10}$, a ferromagnetic metal, by proton irradiation with a stencil mask. An array of 100 nm wide dots of ferromagnetic Co/Pd multilayers was successfully achieved and magnetic measurements showed that the nanostructures have perpendicular anisotropy with coercivity from 1.5 kOe to 2.2 kOe.

Compared to other methods already discussed, this approach allows to produce the reduced $[\text{Co}/\text{Pd}]_{10}$ superlattice with little physical damage. The downside of this relatively new innovation is that the coercivity of reduced superlattice is way smaller than conventional Co/Pd multilayers, which significantly limits the applications in the future.

1.5 Scope

BPM has been considered the candidate to circumvent many of the limitations associated with extending conventional granular media technology. However, fabrication BPM is viewed as the greatest challenge for its commercialization. In this work, a different approach to provide magnetic thin films, multilayers, and nanostructured arrays is introduced, which takes advantage of the exothermic reduction of CoO layer sandwiched between Ta layers annealed at 200 °C. This technique avoids physical removal of magnetic material via argon milling process, which can potentially produce less damaged structures. With this innovative conversion process, we offer a different perspective not only on magnetic films and BPM fabrication, but also on the manufacture of structures consists of metal-metal oxide.

CHAPTER 2 METROLOGY

2.1 Alternating Gradient Force Magnetometer

The alternating gradient force magnetometer (AGFM) is a force magnetometer with possible sensitivity exceeding 10^{-8} emu [31, 32]. It offers 1000 times better sensitivity than a conventional vibrating sample magnetometer (VSM) with comparable working space, and much faster measurements than a SQUID magnetometer [31]. The magnetic property measurements included in this work are performed on a MicroMag 2900 AGM system, as showed in Fig. 2.1, which is located in the Center for Integrated Bio and Nano Systems at University of Houston.

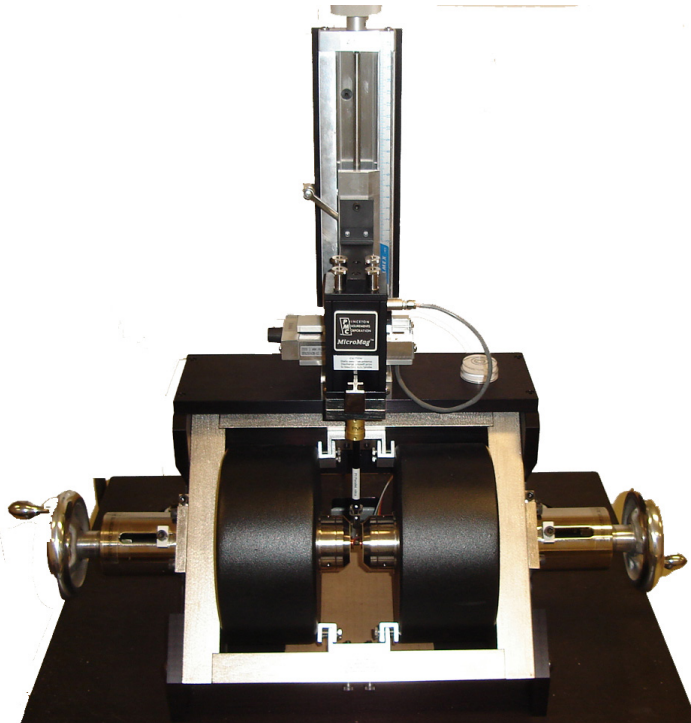


Figure 2.1: A photo of MicroMag AGFM

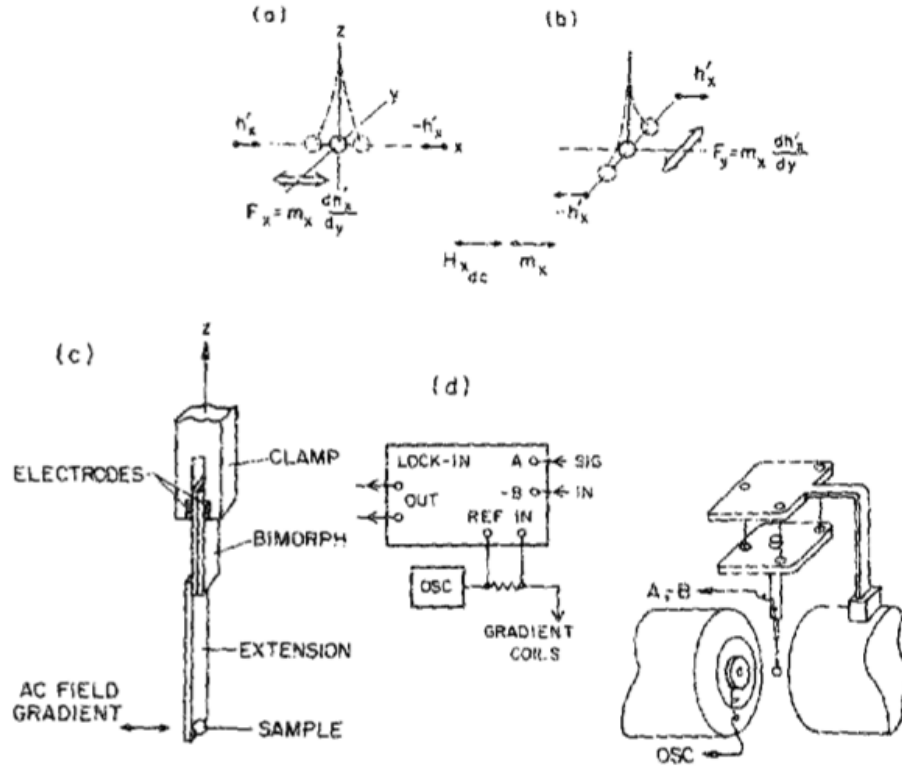


Figure 2.2: Original configuration of Flanders' AGFM

2.1.1 History and Development

A couple of instruments can be called AGFM based on their physical operating forms, since they have been used to study a range of samples under different conditions and geometries. The first AGFM was invented by Zijlstra in 1970 [33], who measured the amplitude of vibration using a microscope. In his design, the alternating gradient field was oriented vertically, in the same direction as the applied DC field, and the displacement of the reed was measured visually, using a calibrated microscope. Reeves also used a similar design but introduced the use of a piezoelectric detector to measure the vibration amplitude. And later on, the sensitivity of the instrument was improved by Roos and Richter, who achieved a sensitivity of 10^{-11} emu [34, 35]. Major improvement in the design were introduced by Flanders, who applied an alternating field with a gradient

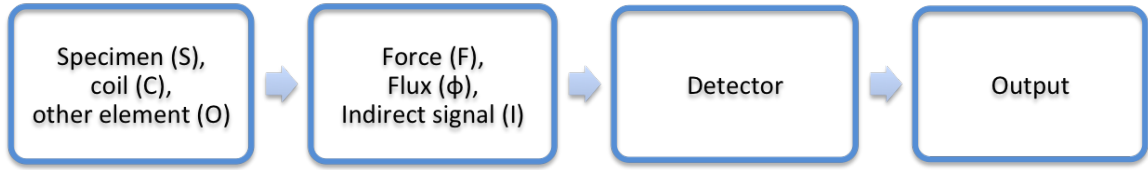


Figure 2.3: General magnetic measurement steps described by Foner

perpendicular to the field vector. This configuration allows the resonant element and piezoelectric biomorph to remain at room temperature, while the sample temperature can vary from 77 to 900 K. The original design is presented here in Fig. 2.2 [31]. In the late 1980's, Princeton Measurements Corp. started commercializing AGFM models, based on a paper by O'Grady [32], in which the resolution and reproducibility was studied. The effect of the alternating gradient field on samples was reported to be considerable in case of samples with a low coercivity, which comes from the sample positioning errors.

2.1.2 General Principles

As illustrated in Fig. 2.3, Foner described a general way to look at magnetic measurement techniques. The specimen produces a force (F), flux (ϕ), or indirect signal (I), which are picked up by detectors and result in a output electrical signal [36]. A sample produces distortion in the field will affect the flux distribution. Methods involve force or flux detection are classified as direct techniques, and all others are labelled as indirect techniques.

A conventional AGFM, as a force magnetometer, has three main components, as explained in Fig. 2.4. First, the instrument must be able to apply a known DC magnetic field to the sample. Secondly, The instrument needs to send a

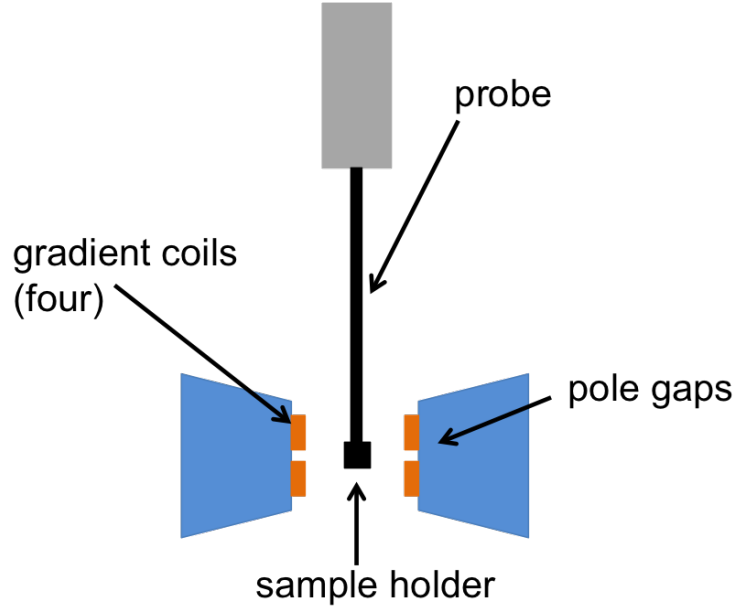


Figure 2.4: Simplified schematic diagram of the main components in a conventional AGFM

controllable alternating field gradient, which can be achieved by placing coils with appropriate geometry with alternating current. Finally, the resulting force, or the displacement produced by the force, has to be detected.

In a real system, the sample is mounted on the tip of a probe, and the other end of which is attached to a piezoelectric element. An alternating field gradient is placed on a magnetized sample, resulting in a periodic force. A bending moment is generated on the piezoelectric element by the force from the alternating field gradient, which generates a voltage proportional to the bending on the probe and force on the sample. The output from the piezoelectric element is read by a lock-in amplifier and the amplitude of the detected voltage is proportional to the magnetic moment of the sample and the magnitude of the gradient field. Detailed calculations and discussions on the theory of operation are provided by Reeves and Flanders [31, 37].

The MicroMag 2900 Model has a modified design that the probe is excited by an alternating field at its mechanical resonance frequency, which greatly im-

proved signal-to-noise ratio. The resonant frequency of the probe and sample depends on the mass of the sample and is generally in the range of 100–1000 Hz. The MicroMag 2009 Model can measure sample with mass up to 100 mg or size up to $4\text{mm} \times 4\text{ mm}$, and has a quoted sensitivity of 10^{-8} emu [32].

2.2 Polar Magneto-optical Kerr Effect Magnetometer

In physics, the magneto-optical Kerr effect (MOKE) is a magneto-optical effect that describes the rotation of polarization of light when reflected from a magnetized surface. MOKE can be further divided into Polar MOKE (PMOKE), Longitudinal MOKE (LMOKE), and Transversal MOKE (TMOKE) by the direction of the magnetization vector of the sample, as illustrated in Fig 2.5. The PMOKE measurement results presented in this work was collected on the PMOKE magnetometer built by Dr. Long Chang from the Center for Integrated Bio and Nano Systems at University of Houston [38].

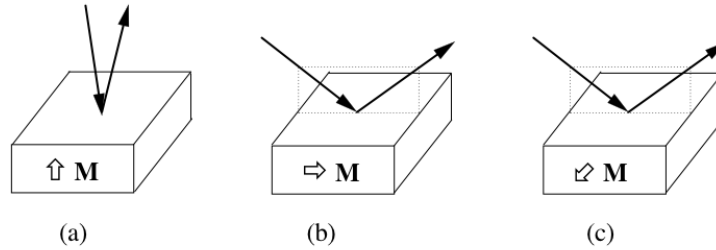


Figure 2.5: Illustration of (a) PMOKE, (b) LMOKE, (c) TMOKE

2.2.1 Polar Magneto-optical Kerr Effect

When light is reflected from a magnetized surface, both the polarization and reflected intensity are changed, due to the optical anisotropy of magneto-optical materials. The source of this optical anisotropy is the magnetization with surface domains, which can be influenced by external forces like magnetic fields.

MOKE can be explained either in a macroscopic perspective by dielectric tensor theory, or in microscopic terms by the spin-orbit interaction theory. In the macroscopic fashion, linearly polarized light experiences a rotation of the polarization plane, Kerr rotation θ_K , and a phase difference between the electrical field components perpendicular and parallel to the incident plane, which is described by the Kerr ellipticity, ε_K . These two quantities are used to form the complex Kerr angel

$$\phi_K = \theta_K + i\varepsilon_K. \quad (2.1)$$

In a more microscopic view, the physical origin of MOKE is the magnetic circular dichroism effect, which explains that the exchange and spin-orbit coupling in a magnetic material give different absorption spectra for left- and right-circularly polarized light. The MOKEs was characterized to be proportional to the magnetization, which makes it particularly useful in the study of magnetism.

2.2.2 Instrument and Measurements

The self-built PMOKE system used in this work is developed mainly for the measurement of BPM. Compared with AGFM and VSM, it is extremely useful for characterizing switching field properties of thin films because it is surface sensitive and requires patterned areas as small as $300 \mu\text{m} \times 300 \mu\text{m}$, so the fabrication time is considerably reduced. However, all the results presented in this work are normalized due to the fact that this system has not been calibrated to provide quantitative magnetic moment values.

In the PMOKE, polarized light reflecting off a magnetized surface experiences a change in polarization angel proportional to the magnetic moment of the film. The detected intensity is

$$I = I_0(1 + 4J_2\theta_K \sin 2\omega t - 4J\varepsilon_K \sin \omega t), \quad (2.2)$$

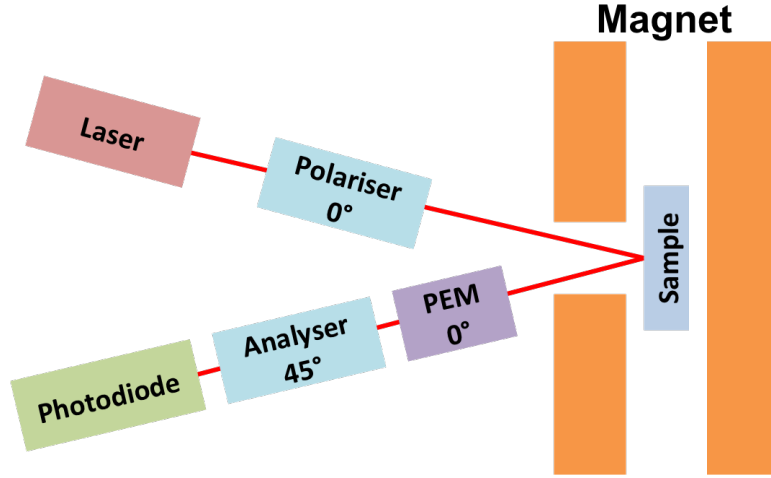


Figure 2.6: Diagram of PMOKE system setup

where I_0 is the laser intensity, θ_K is the Kerr rotation, ε_K is the Kerr ellipticity, and the J_1 and J_2 are Bessel functions of the first and second kind. The Kerr rotation is characterized with considerable speed and sensitivity with a lock-in amplifier tuned to 2ω .

A diagram with key components of the system is showed in 2.6 [38]. The system has a beam size of $206 \mu\text{m}$ and is equipped with a *PatternFinder* to locate the patterned area with micrometer scale resolution.

2.3 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that measures the elemental composition, empirical formula, chemical state, and electronic state of the elements within a material. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analyzed.

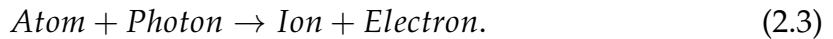
The XPS results from this work were collected using a Physical Electronics model 5700 XPS instrument at a residual pressure of 5×10^{-8} Torr or better.

A monochromatic Al- $k\alpha$ X-ray (1486.6 eV) at 350 W were used as a source, and the photoelectrons were collected at a 45° take off angle with respect to the 0.8 mm analyzed area of sample with a collection solid cone of 5°. All spectra were recorded with applying a pass energy of 11.75 eV that gives an energy resolution better than 0.51 eV.

2.3.1 XPS mechanism

Photoelectron spectroscopy is based on a single photon in/electron out process, that is similar to the photoelectric effect described by Albert Einstein [39]. In XPS, a monochromatic source of X-ray is used to irradiate the sample surface and the photon with certain energy ($h\nu$) is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron.

The overall process of photoionization can be expressed as



And the conservation of energy requires

$$E_{atom} + h\nu = E_{ion} + E_{-e}. \quad (2.4)$$

Since the energy of an atom here is solely presented as kinetic energy (K.E.), and the energy difference between ionized and neutral atoms is generally called the binding energy (B.E.), we can arrange and write the equation as

$$K.E. = h\nu - B.E. \quad (2.5)$$

Another simpler approach is to consider a one-electron model, as illustrated in Fig. 2.7.

The binding energy now is simplified as the energy required to just remove the electron from its initial level to the vacuum level and the process is again given by Equation 2.5.

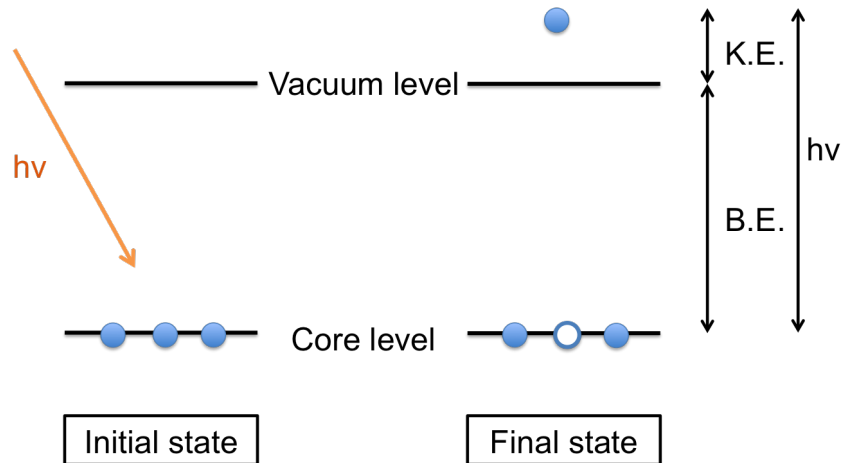


Figure 2.7: Schematic explanation of XPS process

Please note that the binding energies of energy levels in solids are conventionally measured with respect to the Fermi level of the solid, rather than the vacuum level. This introduces a small correction to Equation 2.5 in order to account for the work function of the solid.

2.3.2 Detection and Spectra

Swedish physicist Kai Siegbahn, who later won the Nobel Prize for Physics in 1981, found that chemical environment of an element has small but measurable effects on electron binding energies as measured by XPS, which dramatically increased the value of XPS to surface analysis. For example, the binding energy for the $4f_{7/2}$ electrons in elemental tantalum is at 22.2 eV, while that for the same electrons in tantalum oxide (+5 oxidation state) is at 26.7 eV., as illustrated in Fig.2.8. Such 'chemical shift' is useful to provide not only elemental analysis, but analysis of chemical state of elements as well.

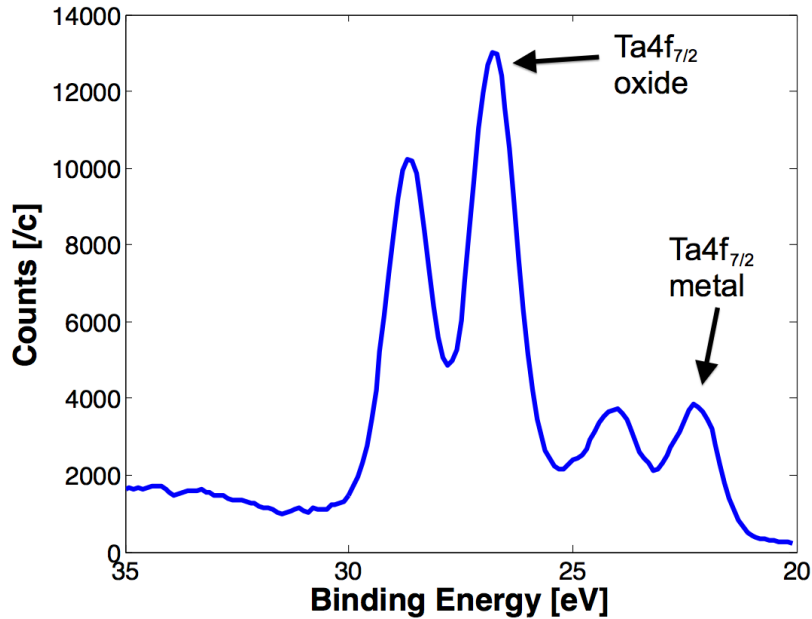


Figure 2.8: A typical XPS spectrum

2.3.3 Advantages and Limitations

Compared with other material science experimental methods, such as X-ray Diffraction and Raman Spectroscopy, XPS has both advantages and limitations.

Advantages

- Relatively non-destructive method of sample characterization;
- Covering by direct study all the elements from Periodic Table except H and He;
- Surface sensitive (Usual probing depth range from 4 nm up to 10 nm);
- Direct chemical bonding information (core levels and valence bands);
- Qualitative and quantitative analysis as well as strong theory support for XPS data interpretation.

Limitations

- Ultra high vacuum system is needed (usually up to 10^{-8} torr);
- Strong local charging of insulating materials under study;
- Lack of information on bulk samples.

2.4 Scanning Electron Microscope

Instead of using light to form an image, scanning electron microscope (SEM) produces images of a sample by scanning it with a focused beam of electrons. Due to the interaction between the electrons from the microscope and the atoms in the sample, a mapping of topography and type of material (i.e., metal or polymer) can be achieved with decent contrast. SEM can provide resolution better than 1 nanometer and covers a wide range of sample specimens, from traditional metals to biological molecules.

2.4.1 Structure and Mechanism

Main components in a conventional SEM, as illustrated in Fig. 2.9 include [40]:

- Electron source ('Gun');
- Electron lenses;
- Sample stage;
- Detectors for all signal of interest;
- Display/ data output devices;
- Infrastructure requirements.

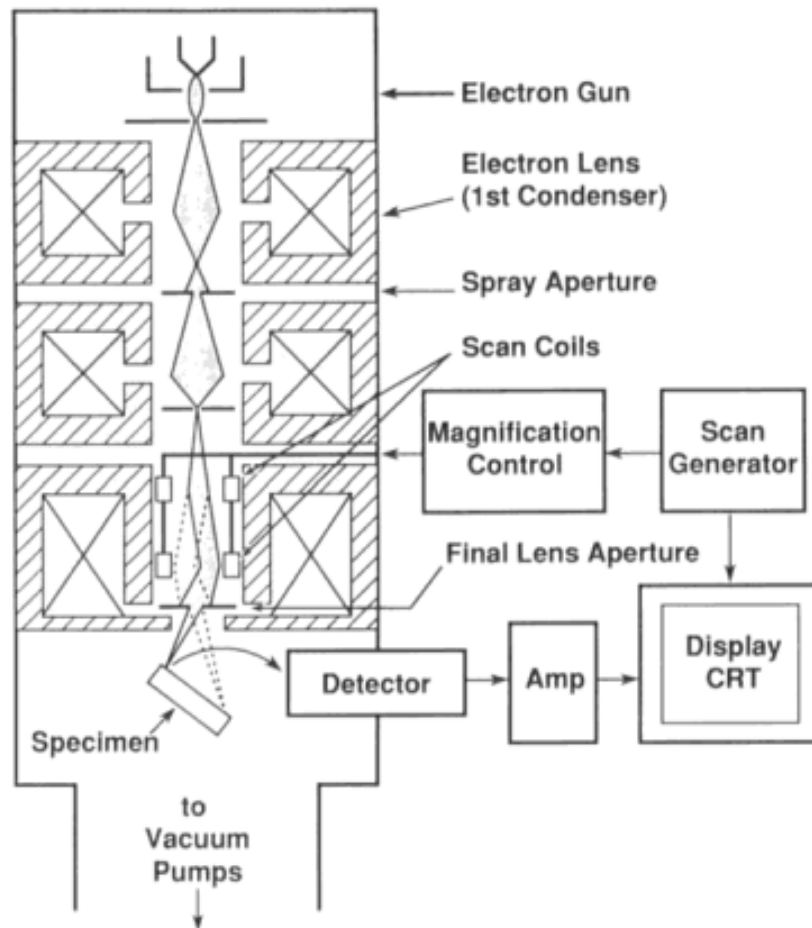


Figure 2.9: Schematic drawing of main components in SEM system

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals due to electron-sample interactions. These signals include secondary electrons that contribute to SEM images, backscattered electrons, diffracted backscattered electrons that are used to determine crystal structures and orientations of minerals, photons (characteristic X-rays that are used for elemental analysis), visible light, and heat. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen, which produces the final image.

The most common mode of SEM is detection of secondary electrons from atoms in the samples that are excited by the electron beam. The number of secondary electrons depends on electron beam energy, as well as the angle at which beam meets surface of specimen, and therefore, by scanning the sample and collecting the secondary electrons with specific detectors, images represents the topography of the surface is created.

2.4.2 Sample Preparation

Sample preparation for SEM is relatively simple compared to other high resolution microscope like transmission electron microscope (TEM). Minimal preparation includes acquisition of a sample that will fit into the SEM stage and electrically conductive surface. Samples should be electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects requires very little special preparation except for cleaning and mounting on a sample holder. For insulator samples, a thin coating of conductive layer, usually gold or graphite, is deposited to prevent the scanning faults and image artifacts caused by charging problem in secondary electron imaging mode.

2.4.3 Strengths and Limitations

SEM is the most commonly used microscope for solid materials in micro- and nano- scale and is critical in all fields that require imaging and characterization of solid materials. Most SEMs are comparatively easy to operate, require minimal sample preparation, and acquire data pretty fast. The limitations of this equipment are the sample size restriction in vertical dimensions (up to a couple of cm), and the requirement of high vacuum environment.

CHAPTER 3 MAGNETIC OXIDES

FABRICATION

A sample fabrication process is designed, considering the limitations of fabrication and metrology systems. This chapter details the exact process used to fabricate three kinds of magnetic oxides for the study. All fabrication process were performed inside the clean room in UH Nanofabrication Facility in order to achieve high-quality, low-defect samples.

3.1 Sputtering Deposition

Thin films are fabricated by the deposition of material atoms on a substrate. A thin film is defined as a low-dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter [41]. Typical deposition techniques include physical vapor deposition (PVD) process such as thermal evaporation, e-beam evaporation, molecular beam epitaxy, sputtering deposition, and chemical vapor deposition (CVD) process that vapor phase of material reacts with other gases or vapors at the substrate to yield nonvolatile reaction products which deposit automatically on the substrate. Among all those techniques, sputtering deposition plays a important role, especially for semiconductor and hard drive disc industry. An important advantage of sputter deposition is that it is capable of depositing materials with high melting points, while evaporation of these materials in a resistance evaporator can be problematic or impossible.

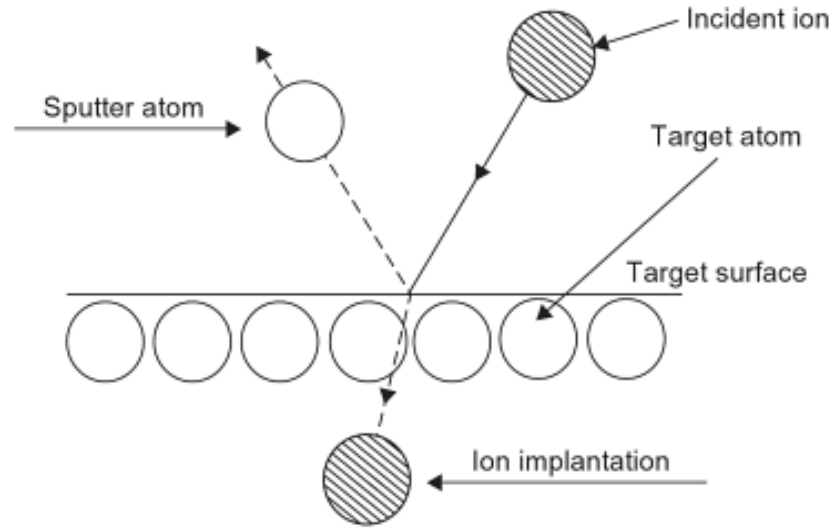


Figure 3.1: Physical sputtering process

3.1.1 Mechanism and System

When a solid surface is bombarded with energetic ions, surface atoms of the solid are scattered backward due to collisions between the surface atoms and the energetic particles, as shown in Fig. 3.1 [41]. Sputtered atoms ejected from the target can fly from the target in straight lines and deposited on the substrates. The gas used to sputter the target materials is often an inert gas like argon. Reactive gases like oxygen or nitrogen can also be used to form compound on the target surface, in-flight or on the substrate depending on the process parameters. Fig. 3.2 illustrates a sputtering chamber with RF powder, which helps to sustain the glow discharge with insulator target.

The sputtering deposition rate is lower than evaporation, and is related to processing pressure, cathode and anode power, substrate position, etc. Generally speaking, reducing sputtering pressure increases the deposition rate. Hence, magnetron-type discharge is introduced to trap electrons into a specific loop in order to increase the collision rate between electrons and the sputtering gas molecules. In this case, a lower sputtering gas pressure is achieved, as well as

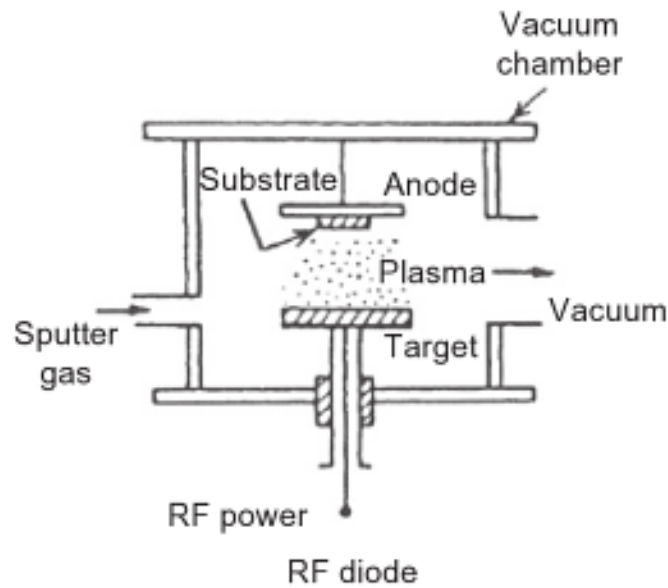


Figure 3.2: RF sputtering system

an increased plasma density, which leads to the increase of current density at the cathode target, effectively increasing the sputtering rate at the target.

3.2 Electron-beam Lithography

Electron-beam lithography, often abbreviated as e-beam lithography, is a fundamental technique of nano fabrication which not only allows direct writing of structures down to sub-10 nm dimensions, but also provides mask templates for other patterning tools such as optical lithography and nanoimprint lithography. It involves the exposure by a highly focused electron beam to dramatically modify the solubility of a resist material during a subsequent development step. Fig 3.3 outlines a typical process using e-beam lithography to form nanoscale patterns in both positive and negative tone resist layers.

E-beam lithography was originally developed in SEM where pattern generator and beam blanker was added to control which area of the viewing field are

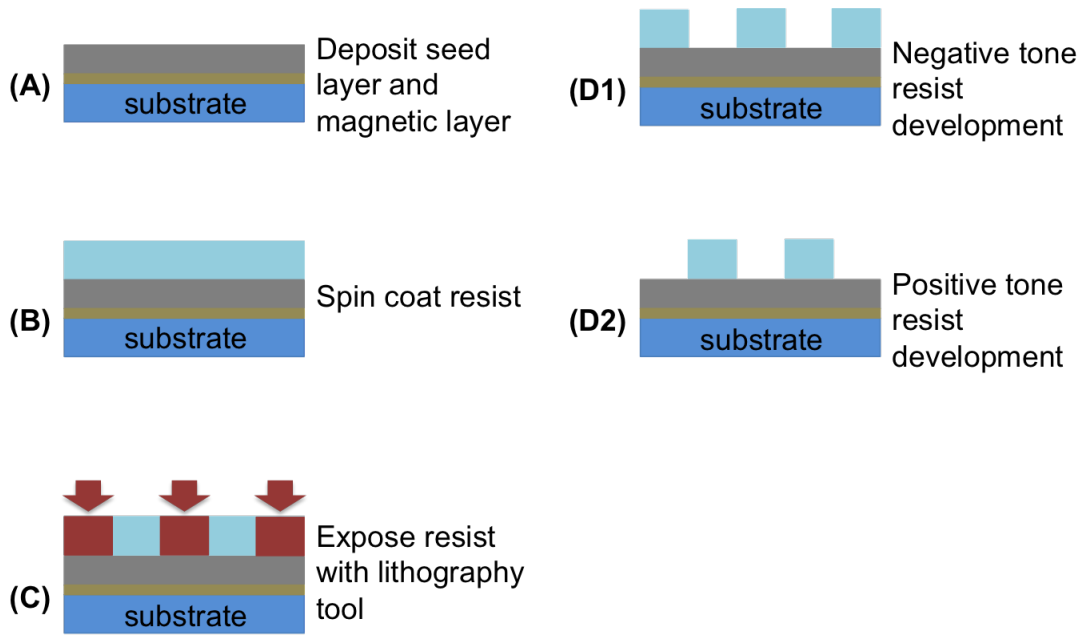


Figure 3.3: Outline of e-beam lithography steps to form nanoscale pattern in both positive and negative tone resist layers

exposed. Modern e-beam lithography tools are fully dedicated to patterning that consists high brightness electron sources for faster throughput and high resolution mechanical stages to be able to expose step-by-step large substrates under the relatively narrow field of focus of the electron beam. The key objectives of e-beam lithography systems are to achieve arbitrary patterns with high resolution, high density, high sensitivity and high reliability.

3.2.1 Resists, Exposure, and Sensitivity

Inelastic collisions of electrons with the resist result in ionization, which is accompanied by physical-chemical changes in the resist. Just like traditional optical lithography, e-beam lithography has two types of resists. Positive tone resists go through a conversion from low to high solubility upon exposure to electrons. A classic example is PMMA (poly-methyl methacrylate), a long chain polymer, breaks into smaller, more soluble fragments by the electron beam. On the contrary, in negative tone resists, the electron convert the material to low solubility.

Table 3.1: Commonly used resists for e-beam lithography

Resists	Tone	Critical Dose (in $\mu\text{C} / \text{cm}^2$)
PMMA	positive	500
	negative	>10000
HSQ	neative	800
ZEP	positive	30
PHOST	negative	8500
PMGI	positive	1000

HSQ (hydrogen silsesquioxane) undergoes a cross-linking reaction to become larger, less soluble polymers.

Different resists require different critical dose, the amount of electron beams, to change the solubility during the exposure process, and they respond quite differently to the change of dose. Special resist like PMMA can be used as both positive and negative tone resists, depending on the dose it being exposed to. Table 3.1 lists several commonly used resists for e-beam lithography.

3.2.2 Advantages and Limitations

As a direct writing system, e-beam lithography tools are capable of providing extremely high resolution features and arbitrary patterns without masks. They also break the diffraction limit which exists in optical systems, and are capable of fabricating features in nanoscale regions. Their disadvantage is the long time taken to write large, complex pattern, when features might be affected by beam drift or instability that occur during the long exposure process. In addition, proximity effect has to be considered, which attributes to the fact that electrons undergo multiple inelastic and elastic scattering collisions from substrate. Some energy is transferred to the proximity of the desired area, leading to unwanted, less sharp features generated after development. Specific settings with smaller beam spot size and higher acceleration voltages can be used to limit the proxim-

ity effect.

3.3 Pattern Transfer

Argon milling is used to transfer the resist pattern into the magnetic film. This process physical removes material indiscriminately by blasting the sample with a broad beam of argon atoms. The region not protected by the resist is milled away, resulting in a replication of the resist pattern in the magnetic film.

The milling rate varies between materials. Generally, we measure the rate of polymers twice as that of metals. The milling rate of metal is measured by covering half of sample with resist (HSQ used in this study) and perform argon mill for 5 min. The resist is then removed by hydrofluoric acid and the step between the covered and uncovered region shows the thickness of metal being milled. The milling rate for polymers can be calculated accordingly.

3.4 Thin Films and Multilayers Deposition

Ta(15 nm)/CoO(10 nm)/Ta (5 nm) thin film stacks and Ta(15 nm)/[CoO(0.3 nm)/Pd(0.7 nm)]_N/Ta(5 nm) multilayer stacks were deposited using a AJA ATC 2200 ultra high vacuum DC magnetron sputtering system. The base pressure was set as 5×10^{-8} Torr, and the processing pressure was kept to be 5×10^{-3} Torr. CoO thin films were deposited by reactive magnetron sputtering with argon (35 sccm), and oxygen (5 sccm), under 100 W DC power and 50 W RF power; all other materials (Co, Pd, Ta) were deposited by sputtering with argon (35 sccm). The sample holder position was 40 mm on the ruler and set to rotate during all the sputtering process. The sputtering rates for different materials are listed in Table 3.2 respectively.

Table 3.2: Sputtering rates

Materials	Sputtering Rates [$\text{\AA}/\text{s}$]
Ta	0.94
Co	0.6
CoO	1.12
Pd	1.7

3.5 Nanostructured Arrays

Patterns were produced on Ta(15 nm)/[CoO(0.3 nm)/Pd(0.7 nm)]_N/Ta(5 nm) multilayers by exposing 120 nm HSQ resist using a JEOL JBX 5500FS eBeam Writer. A lithography condition of 1nA and a dose of 900 $\mu\text{C}/\text{cm}^2$ were used, followed by a 1 minute developing process in 25 % Tetramethylammonium hydroxide (TMAH) solution. The resist pattern was transferred into the film via argon ion milling and examined by FEI XL-30FEG scanning electron microscope (SEM). A 40° tilted SEM image of patterned and milled 180 nm square array is showed in Fig. 3.4. A considerable redeposition of sputtered metals on the side walls of HSQ resist was observed.

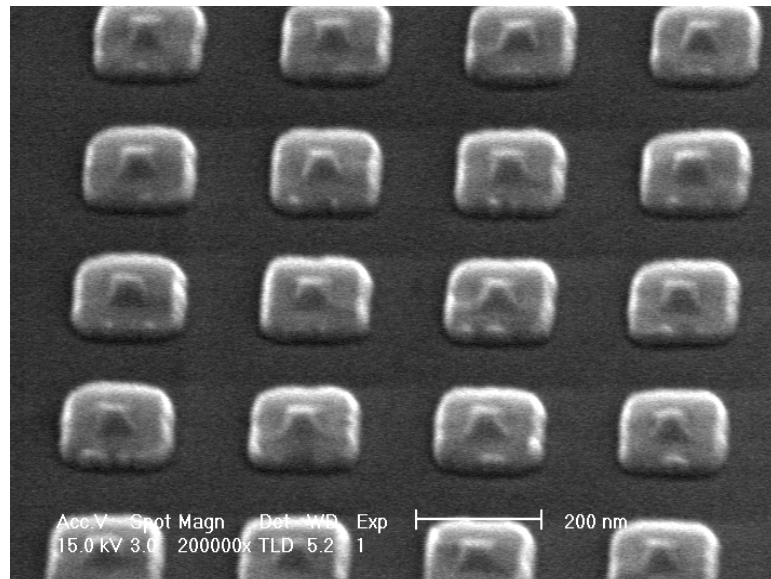


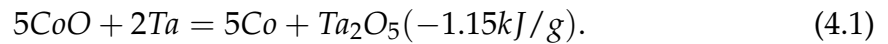
Figure 3.4: Nanostructured array of 180 nm squares

CHAPTER 4 RESULTS AND DISCUSSION

With the help of the gettering property of Ta, nonmagnetic thin films of CoO sandwiched between Ta seed and capping layers can be effectively reduced to a magnetic cobalt thin film by annealing at 200 °C, whereas CoO does not exhibit ferromagnetic properties at room temperature and is stable at up to ~ 400 °C [42]. In this chapter, the gettering property of Ta-CoO system is well examined. Results of converted ferromagnetic thin films, multilayers, and nanostructured arrays are presented and the potential applications using this technique are discussed.

4.1 Thermodynamic Calculations

To investigate the Ta-CoO system, a thermodynamic calculation is performed by Chamath Dannangoda from University of Texas - Brownsville, using the thermochemical computer code HSC Chemistry-7, which includes minimization of the Gibbs free energy subject to mass and energy balances [43, 44]. The dependence of the adiabatic temperature and the equilibrium concentration of solid and liquid phases on the cobalt oxide concentration for the system studied is shown in Fig. 4.1. In this energetically favorable reaction, Ta is oxidized in a process that is similar to the ones exhibited by thermite nanocomposites [45], and the reaction can be generalized as



With the increasing amount of CoO, Ta(S) is consumed until it reaches the stoichiometric point (50.86%). The adiabatic temperature rises up to 2150 K during this process and reaches a plateau. When the amount of CoO is higher than the stoichiometric point, excess amounts of CoO can be seen and the adiabatic

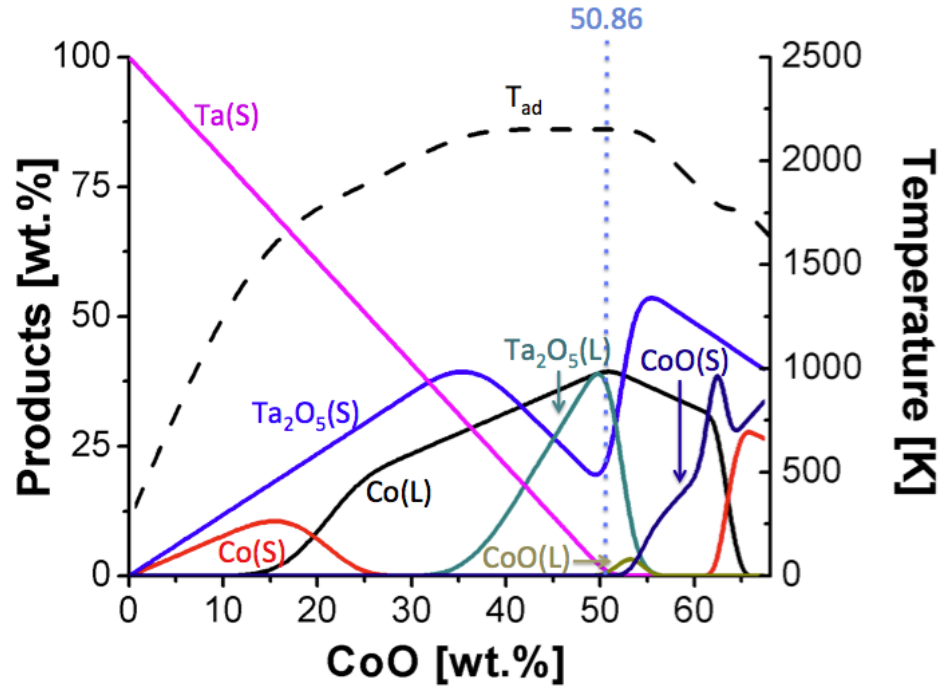


Figure 4.1: Dependence of the maximum adiabatic temperature and equilibrium concentration of condensed phases on cobalt oxide concentration; (S) and (L) denote solid and liquid states, correspondingly.

temperature begins to decrease, converting liquid Ta_2O_5 to its solid state. Significantly, the thermodynamic calculations confirm the possibility of an exothermic interaction between CoO and Ta without generating any gaseous phases.

4.2 Converting Magnetic Oxides Thin Films into Ferromagnetic Thin Films

4.2.1 Hysteresis Loops and Magnetic Measurements

To study the role of the Ta gettering layer in the conversion process, a sample of film stacking Ta(15 nm)/CoO(10 nm)/Ta (5 nm) was prepared, as illustrated in Fig. 4.2. The saturation magnetization (M_s) of 10 nm CoO thin film annealed at different temperatures for 5 min is shown in Fig. 4.3(a). An increase of M_s

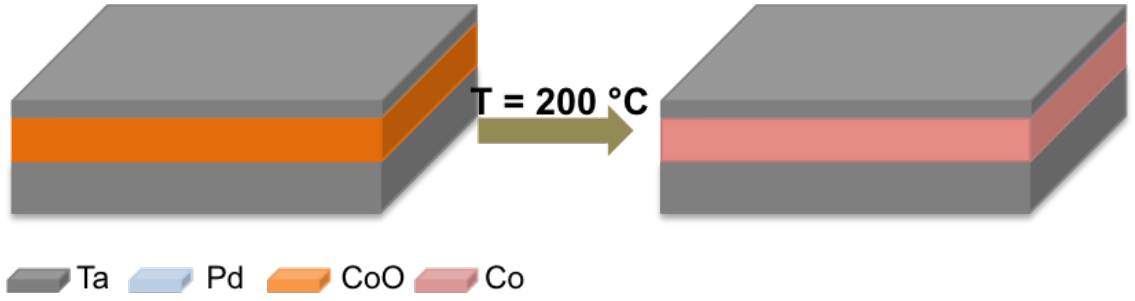


Figure 4.2: Schematic diagram of converting CoO to Co using Ta gettering layers

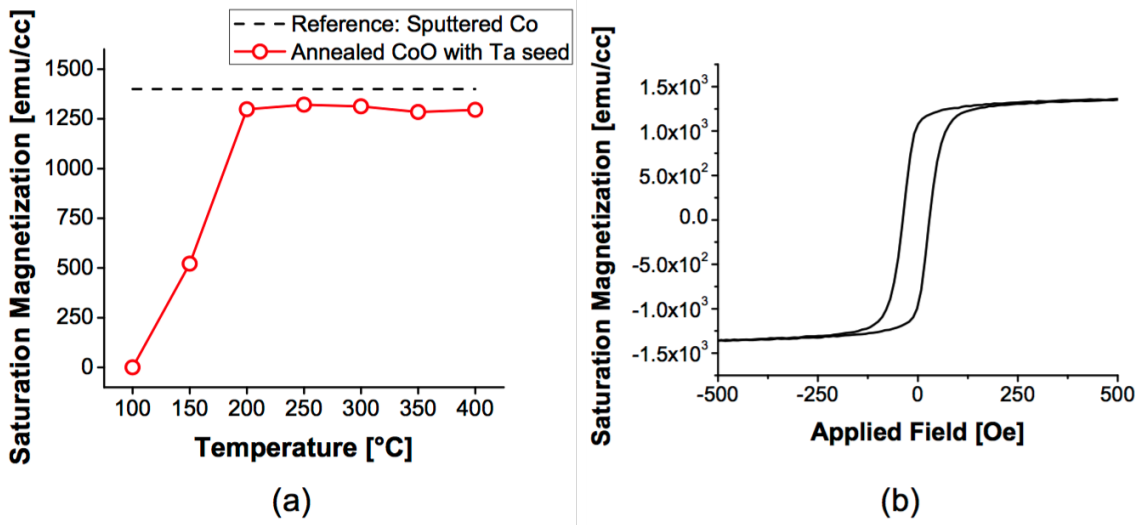


Figure 4.3: (a) M_s of annealed CoO thin film sandwiched between Ta seed and capping layers depending on annealing temperature in air. (b) Hysteresis loop of annealed CoO thin film.

from 0 to 1300 emu/cc at a temperature as low as 200 °C was observed. The M_s of annealed CoO approaches the M_s of sputtered Co thin film as the temperature approaches 200 °C; no changes were observed at annealing temperatures beyond 200 °C. The hysteresis loop of CoO thin film annealed at 200 °C for 5 min is showed in Fig. 4.3(b). For comparison, the same experiments were performed on samples without Ta gettering layers, and no ferromagnetic properties were observed.

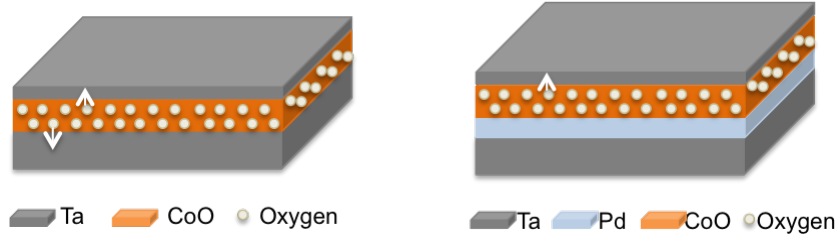
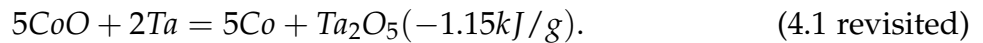


Figure 4.4: Schematic diagram of thin film structures before and after inserting Pd layer

4.2.2 XPS analysis

Further study of the conversion process mentioned in Equation 4.1 was performed on XPS, which provided insightful information regarding elemental compositions and chemical states. Due to the fact that XPS is surface sensitive, a 6 nm Pd layer is inserted between the Ta seed layer and the CoO layer to block the reduction of CoO by the Ta seed layer, and the annealing was conducted inside the XPS ultra high vacuum chamber. The structure before and after inserting Pd layer is shown in Fig. 4.4. In this case, conversion between the Ta capping layer and the CoO layer is analyzed without possible background gases. Fig. 4.5 presents the Ta4f spectra of film stack Ta(15 nm)/Pd(6 nm)/CoO(10 nm)/Ta(5 nm), before and after 200°C annealing, respectively. The disappear of Ta4f (metal phase) peaks indicates the oxidation of Ta during low temperature annealing, as suggested in reaction



The same sample was treated under a built-in Ar^+ gun to sputter off 5 nm Ta from the surface. Thus, CoO thin films underneath were exposed and similar XPS analysis were performed on Co2p peak region, as shown in Fig. 4.6. Before annealing, typical CoO peaks, along with their satellite peaks, can be easily identified [46, 47, 48]. Sharp Co (metal phase) peaks are observed at ~ 778 eV after annealing, which represents the reduction of CoO during low temperature

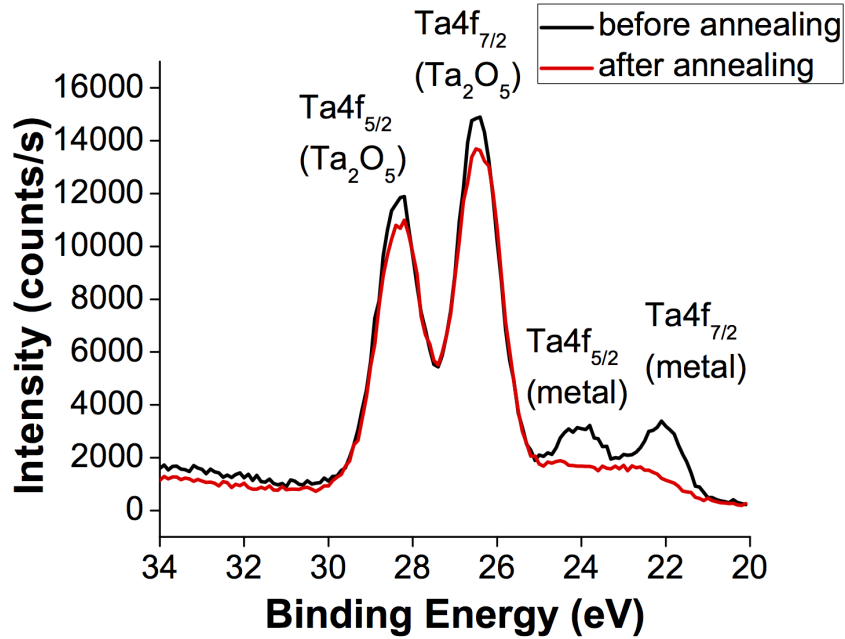


Figure 4.5: XPS spectra of Ta4f

Table 4.1: Summary of XPS Peak Positions

chemical states	peak position [eV]			
	oxide phase		metal phase	
	this work	reference	this work	reference
Ta4f _{7/2}	26.6	26.4 – 26.8	22.1	21.5 – 22
Ta4f _{5/2}	28.4	28.3 – 28.7	24.3	23.4 – 23.9
Co2p _{3/2}	781	780.2 – 780.5	778.5	778 – 778.4
Co2p _{1/2}	797	796 – 796.3	793.5	793.2 – 793.6

annealing. However, the mix of both oxide and metal phases showed in these two spectra might suggest an incomplete conversion process.

A summary of peak positions of Ta4f and Co2p is listed in Table 4.1, along with typical peak positions of those chemical states as references.

4.2.3 Limitations of Conversion

In previous XPS results, shown in Fig. 4.6, we have noticed that not all CoO was converted to Co when we blocked the reaction with Ta seed layer. There are a couple of explanations, one reason being that 5 nm Ta capping layer was

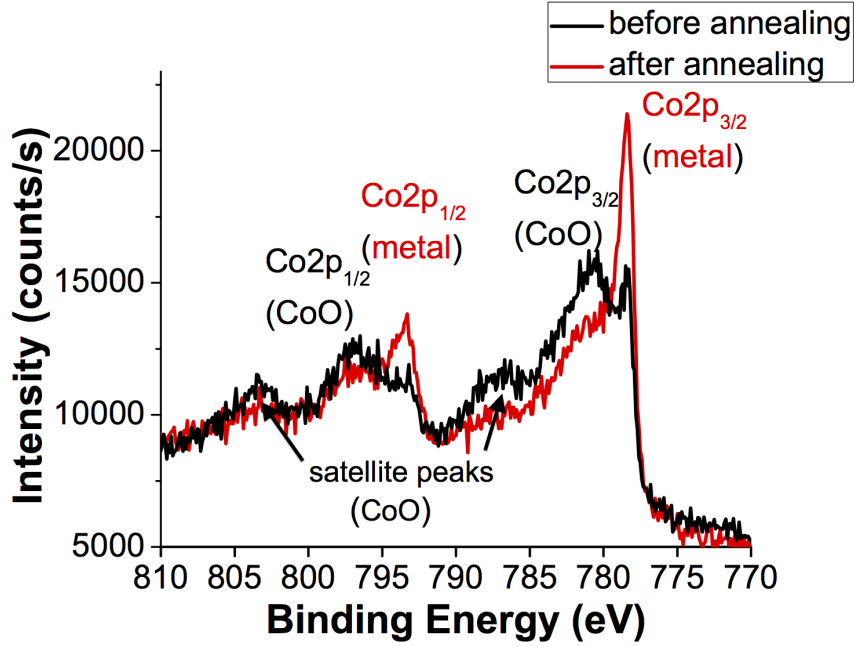


Figure 4.6: XPS spectra of Co2p

not sufficient to get all the oxygen from 10 nm CoO layer. Other reasons can be the inadequate annealing time, Ta oxidation with background gases, or poor diffusion length of oxygen atoms in CoO. To explore the limitation of this conversion process, two sets of different film stacking were prepared and their magnetic properties are analyzed.

CoO Thickness Limitations

In film stacking of Ta(15 nm)/Pd(6 nm)/CoO(10 nm)/Ta(5 nm), the oxygen atoms near Pd/CoO interface need to diffuse through 10 nm CoO in order to react with Ta capping layer, as showed in Fig. 4.4. Triggered by low temperature annealing, some oxygen atoms closer to the Ta capping layer were able to break Co-O bonds and diffused into Ta, forming Ta₂O₅. By changing Ta capping layer thickness to 100 nm and annealing the films at 200°C for 24 hours, we were able to find the limitation of diffusion length of oxygen atoms, assuming having adequate energy to kick off the reaction and sufficient Ta to react with.

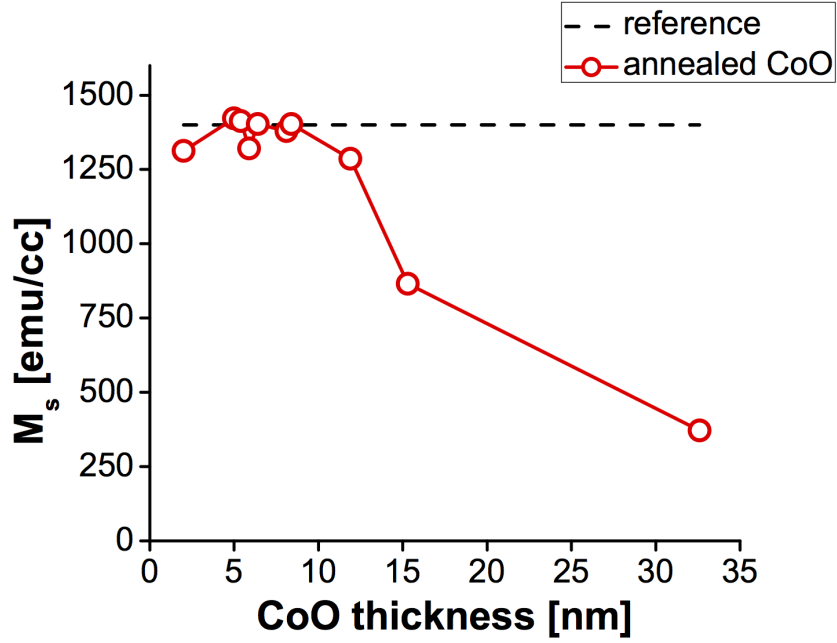


Figure 4.7: M_s of annealed Ta(15 nm)/Pd(6 nm)/CoO/Ta(100 nm) with CoO different thickness

Fig. 4.7 shows the M_s values of annealed modified film stacking Ta(15 nm)/Pd(6 nm)/CoO/Ta(100 nm) remain close to the M_s of sputtered Co film when CoO film thickness is less than ~ 12 nm. Beyond that thickness, a drastic decrease of M_s values were observed. This indicates that the oxygen atoms in CoO film can diffuse through 12 nm at most in the system studied, given sufficient Ta and time. In other words, the conversion of CoO thin films with only one side of Ta layer, instead of a sandwich structure, is limited within 12 nm.

Annealing Time Limitations

In the theory of thermodynamics and kinetics, a reaction must have energy input before it can proceed; otherwise, the reactants cannot cross the activation energy threshold and convert to products. In our work, it is natural to consider the low temperature annealing to be the source of energy, and longer annealing time represents more energy input. However, due to the layer structure, reactants

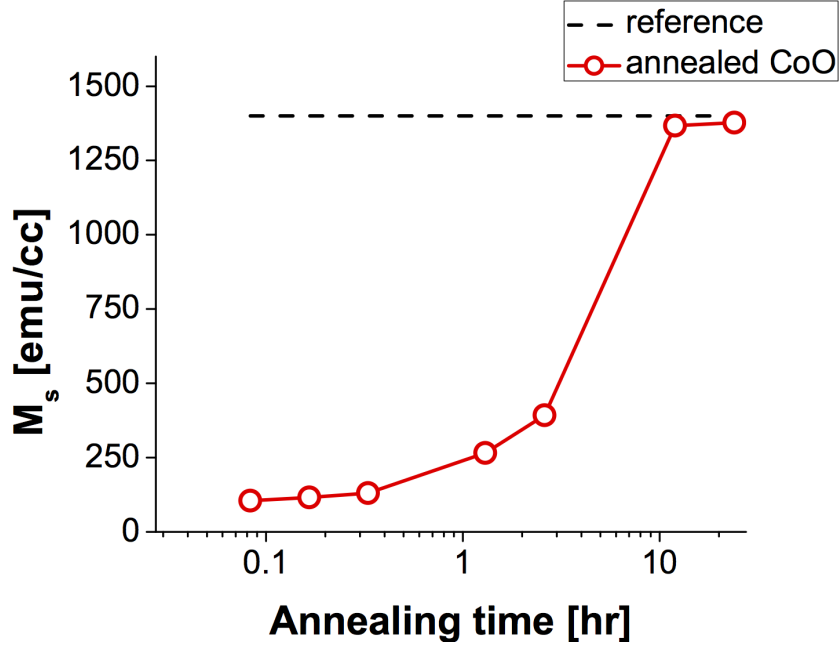


Figure 4.8: M_s of Ta(15 nm)/Pd(6 nm)/CoO(10 nm)/Ta(100 nm) with different annealing time

(CoO and Ta) have considerably limited surfaces for reaction, and thus the activation energy threshold can be different for CoO in different depths, closer to or further away from the Ta layer. Fig. 4.8 shows the influence of annealing time on M_s values of film stacking Ta(15 nm)/Pd(6 nm)/CoO(10 nm)/Ta(100 nm), when annealed in a vacuum oven at 200°C. An increasing M_s value was observed until it saturated at 12 hours, meaning all 10 nm CoO was converted to Co. This result is very different from Fig. 4.3(a), which indicates 5 min annealing is enough to reduced 10 nm CoO sandwiched between Ta layers; this difference is likely due to the change of film structure and oven type (from conventional oven to vacuum oven).

Oxygen Diffusion Length in CoO

As stated in Equation 1.2, the diffusion length of oxygen can be estimated by

$$t \approx \frac{x^2}{2D}, \quad (1.2 \text{ revisited})$$

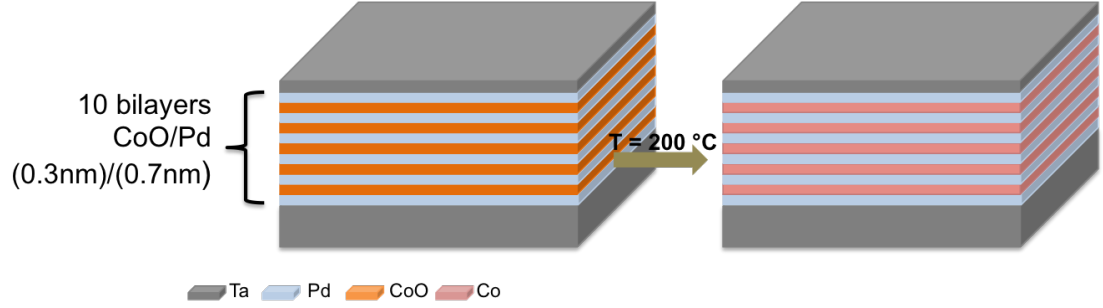


Figure 4.9: Diagram of CoO/Pd multilayer structure studied in this work

where the diffusion time t is 24 hours, and diffusion coefficient D in metals is reported to be typically in the order of $10^{-21} \text{ m}^2\text{s}^{-1}$. The estimation diffusion length calculated for the condition used in this experiment is $\sim 13 \text{ nm}$. To acquire a better estimation, accurate value of diffusion coefficient and the activity of Co atoms need to be considered.

4.3 Application of Low Temperature Conversion in Multilayers

In the previous chapter, we have demonstrated that a nonmagnetic thin film of CoO, sandwiched between Ta seed and capping layers, can be effectively reduced to a magnetic Co thin film by annealing at 200°C . The limitations of this system have also been discussed. Driven by the this observation, CoO has been introduced into the Co/Pd multilayer system to further study the fidelity of this technique. Fig. 4.9 shows the structure of the multilayer stack before and after low temperature annealing.

4.3.1 Hysteresis Loops and Magnetic Measurements

$[\text{Co}/\text{Pd}]_N$ multilayers have been studied extensively as a candidate material for high-density magnetic recording, promising areal densities beyond $1 \text{ TB}/\text{in}^2$

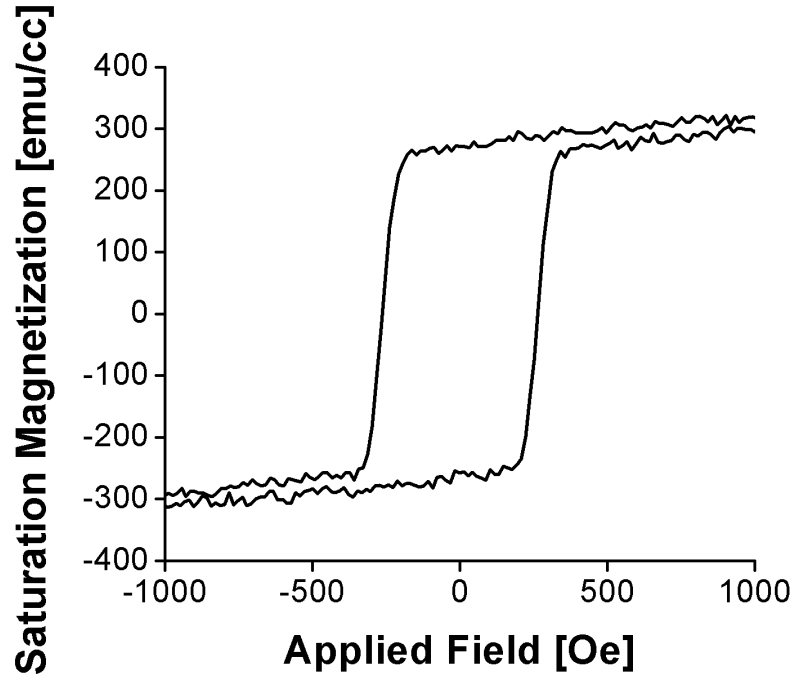


Figure 4.10: Hysteresis loop of Ta/[CoO/Pd]₁₀/Ta multilayers after annealing

[49, 50, 51, 52]. [Co/Pd]_N multilayers exhibit strong perpendicular magnetic anisotropy and high saturation magnetization, tunable through manipulating the seed layer, individual Co and Pd layer thickness, number of layers, and deposition conditions [51, 52, 18, 22].

The deposition parameters for an optimized high magnetic anisotropy [Co/Pd]₁₀ multilayer with composition Ta(15 nm)/Pd(0.7 nm)/[Co 0.3 nm)/Pd(0.7 nm)]₁₀/Ta(2.5 nm) were used to deposit Ta/[CoO/Pd]₁₀/Ta multilayers, where oxygen was introduced during Co layers deposition steps. As deposited, [CoO/Pd]₁₀ multilayers did not exhibit ferromagnetic properties. However, a strong onset of ferromagnetic properties was observed upon annealing the [CoO/Pd]₁₀ multilayers in air at ~200°C for 5 min, and the hysteresis loop is showed in Fig. 4.10.

Fig. 4.11 and Fig. 4.12 describe the influence of annealing temperature and annealing time on the conversion of [CoO/Pd]₁₀ multilayers. The M_s of

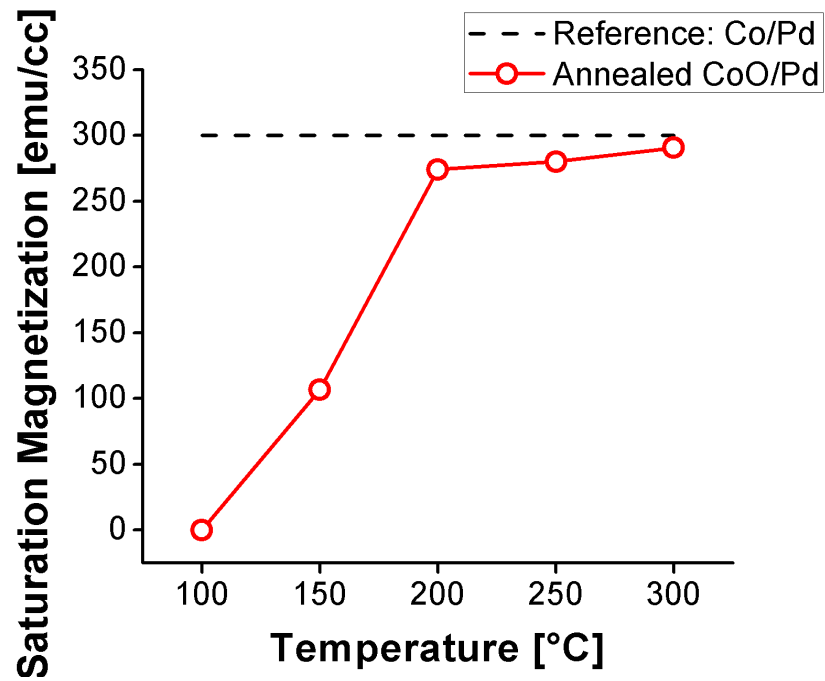


Figure 4.11: Influence of annealing temperature on the M_s of Ta / [CoO/Pd]₁₀ / Ta multilayers

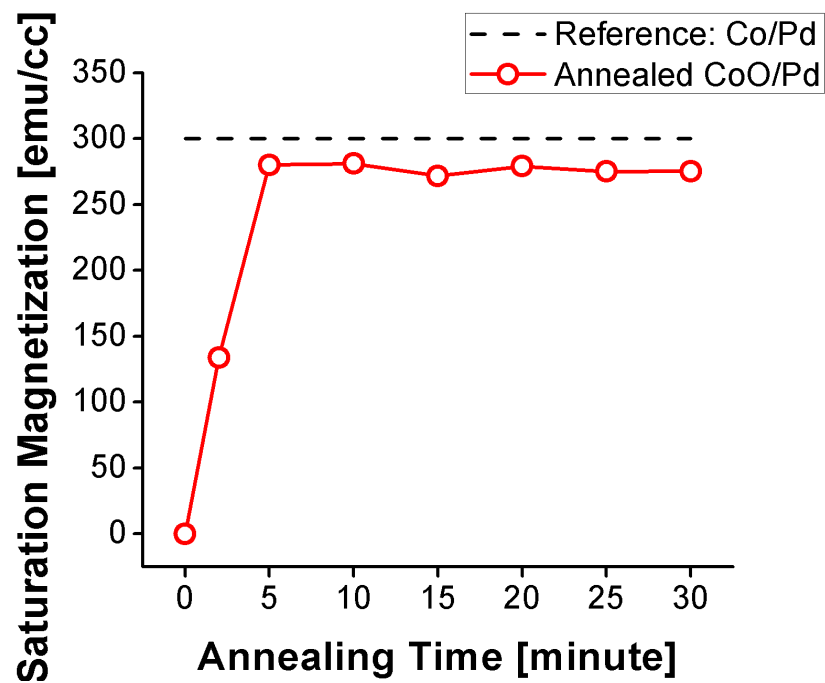


Figure 4.12: Influence of annealing time on the M_s of Ta / [CoO/Pd]₁₀ / Ta multilayers

[CoO/Pd]₁₀ approaches the M_s of sputtered [Co/Pd]₁₀ when annealed at 200°C for 5 min. Because the magnetic properties of Co/Pd multilayer films are controlled by the interfacial effects between Co and Pd layers, it is evident that [CoO/Pd]₁₀ transformed to [Co/Pd]₁₀, with decent interface structure. Judging from the M_s of annealed [CoO/Pd]₁₀, annealing at temperatures below 200°C shows a partial conversion of CoO to Co, while annealing at temperatures above 200°C resulted in a complete conversion. Annealing the multilayers at temperature higher than 200°C for 5 min, or annealing for longer than 5 min at a temperature of 200°C does not increase the M_s . All these results are in accordance with what we observed from low temperature conversion of thin films, and are attributed to the presence of Ta in the film stack via its gettering property.

4.3.2 Magnetic Anisotropy and Switching Properties

As already explained, the magnetic anisotropy expresses the tendency of the magnetization to lie along certain directions in a magnetic material and has a couple of sources, such as magnetocrystalline anisotropy, shape anisotropy, magnetoelastic anisotropy, and exchange anisotropy. Co/Pd multilayer structure has a strong magnetoelastic anisotropy, arising from the asymmetrical environment at Co/Pd interfaces. However, the domain wall motion, triggered by defects or certain microstructures in the material, prevent us from observing the true value of magnetic anisotropy in the thin film [53]. To avoid the effect of domain wall motion, a set of annealed CoO/Pd multilayers were patterned into an array of 200 nm square pillars spaced 400 nm apart by e-beam lithography tool mentioned in Chapter 3, and approximately 200 μm to the side of this array, a solid 500 μm $\times$ 500 μm square of CoO/Pd multilayer was made as a control. Multilayer films consisting of Ta(15 nm)/Pd(0.7 nm)/[CoO/Pd(0.7 nm)]₁₀/Ta(5 nm) were prepared, where the CoO layer thickness was varied from 0.3 to 0.9 nm, while the Pd layer

thickness was kept constant at 0.7 nm. Patterning stops magnetization reversals triggered by domain wall motion, enabling the comparison of the true magnetic anisotropies in the annealed films.

A series of hysteresis loops comparing the switching properties of $[\text{Co}/\text{Pd}]_{10}$ multilayers, annealed $[\text{CoO}/\text{Pd}]_{10}$ multilayers, and a set of annealed and then patterned $[\text{CoO}/\text{Pd}]_{10}$ multilayers is shown in Fig. 4.13. A 40° tilted SEM image of the patterned square array is shown in Fig. 4.13 inset. The control pattern does not have a hysteresis loop after patterning, confirming that heat generated from the lithography process is not sufficient to convert the film. After annealing, the control pattern becomes ferromagnetic with a coercivity of approximately 500 Oe, showed as green loop in Fig. 4.13. The hysteresis loops of the annealed patterned films have coercivities ranging from 1 to 2.5 kOe. The change in the switching properties of the converted continuous and patterned $[\text{CoO}/\text{Pd}]_{10}$ multilayers is significant and resembles typical Co/Pd multilayers, showed as blue loop in Fig. 4.13.

4.3.3 Bilayer Limitations

As we already discussed, the oxygen atoms in CoO need to diffuse through certain amount of distance in order to react with Ta layers. In film stacking of $\text{Ta}(15 \text{ nm})/\text{Pd}(0.7 \text{ nm})/[\text{CoO}(0.3 \text{ nm})/\text{Pd}(0.7 \text{ nm})]_N/\text{Ta}(2.5 \text{ nm})$, oxygen atoms need to diffuse through CoO layers, as well as Pd layers. To study the behavior of oxygen atoms in the $[\text{CoO}/\text{Pd}]_N$ multilayer system under low temperature annealing, a 6 nm Pd layer is inserted between the Ta seed layer and the $[\text{CoO}/\text{Pd}]_N$ multilayers to block the reduction of CoO by the Ta seed layers. In other words, oxygen atoms will have to diffuse up through CoO/Pd layers and react with the Ta capping layer on the surface. The M_s of annealed $\text{CoO}(0.3 \text{ nm})/\text{Pd}(0.7 \text{ nm})$ multilayers on a $\text{Ta}(15 \text{ nm})/\text{Pd}(6 \text{ nm})$ seed layer as a function of CoO/Pd bilayer

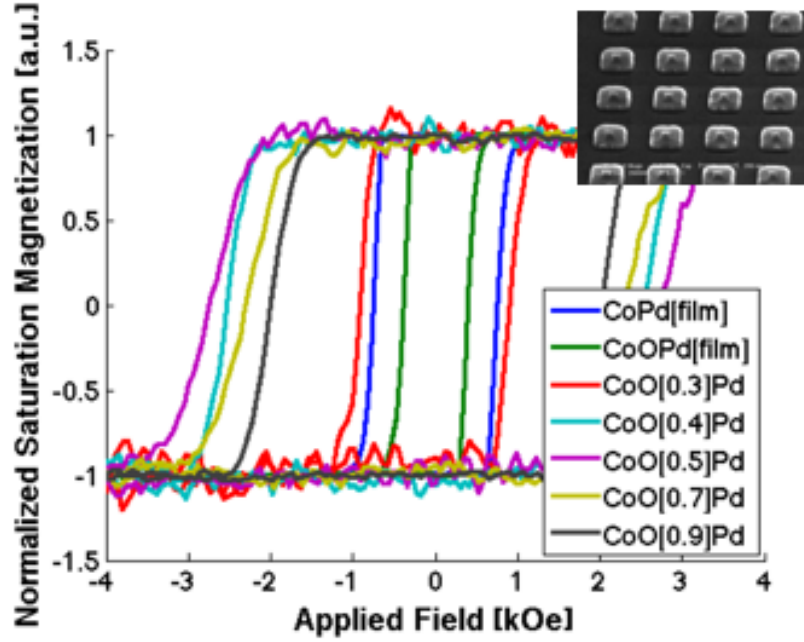


Figure 4.13: Comparison of the hysteresis loops of $[\text{Co}/\text{Pd}]_{10}$ film, annealed $[\text{CoO}/\text{Pd}]_{10}$ film, and annealed then patterned $[\text{CoO}/\text{Pd}]_{10}$ films with different Co layer thickness

repeats is shown in Fig. 4.14. The trend shows that the 2.5 nm of Ta capping layer does not completely convert 10 bilayers of CoO/Pd. At 5 bilayers and below, the saturation magnetization approaches 300 emu/cc, which is equivalent to Co/Pd films. This implies that the effective range for complete conversion of CoO/Pd using Ta is approximately 5 nm. At distances beyond 5 nm, it is hypothesized that the conversion percentage gradually decreases to zero.

4.4 Application of Low Temperature Conversion in Nanostructured Arrays

In previous chapters, we have discussed the use of Ta gettering layers for low temperature conversion in CoO thin films and CoO/Pd multilayers. Since Ta is essential for this conversion process, a new technique of patterning magnetic nanostructured arrays is proposed here. By patterning only the Ta capping

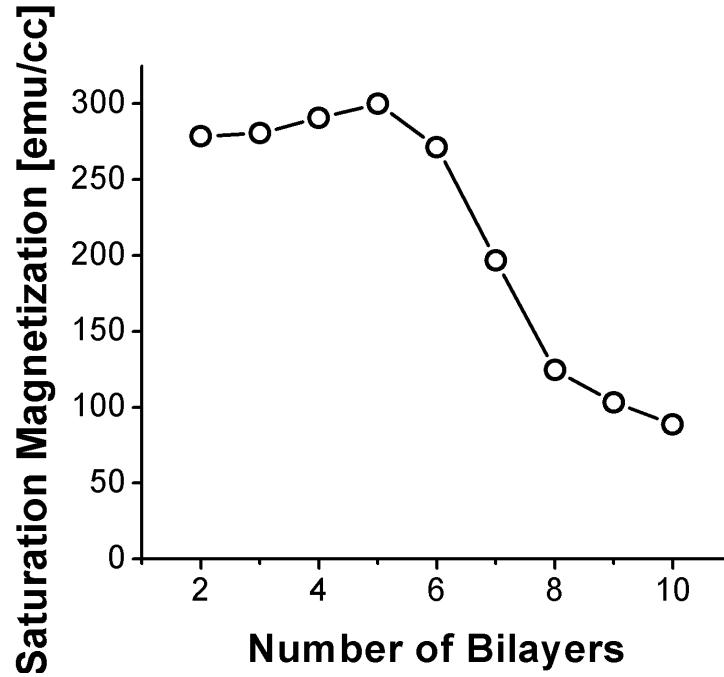


Figure 4.14: M_s of annealed CoO/Pd films varies with the number of bilayer repeats.

layer, CoO/Pd can be locally converted to Co/Pd upon low temperature annealing, as illustrated in Fig. 4.15. Ta islands serve as catalysts for the conversion process, enabling only the CoO in the vicinity to reduce to Co. When tried on $[\text{CoO/Pd}]_N$ multilayers, this process creates ferromagnetic $[\text{Co/Pd}]_N$ islands in a sea of nonmagnetic $[\text{CoO/Pd}]_N$.

4.4.1 Hysteresis Loops and Magnetic Measurements

Considering the bilayers limitation, Ta(15 nm)/Pd(6 nm)/[CoO(0.3 nm)/Pd(0.7 nm)]₅/Ta(2.5 nm) film stack was prepared and the Ta capping layer was patterned into an array of 200 nm squares spaced 400 nm apart by e-beam lithography and argon ion milling. Approximately 200 μm to the side of the array pattern is a control pattern, 500 μm $\times$ 500 μm . After annealing at 250 $^{\circ}\text{C}$ for 5 min, the structure of ferromagnetic $[\text{Co/Pd}]_5$ islands in a matrix of nonmagnetic $[\text{CoO/Pd}]_5$ film was achieved. The hysteresis loops for these $[\text{Co/Pd}]_5$ islands

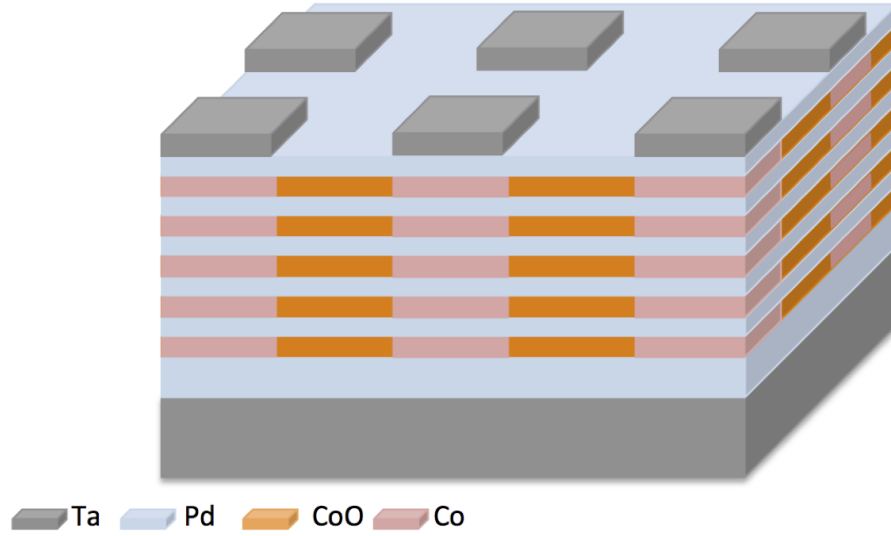


Figure 4.15: Schematic diagram portrays the BPM fabrication strategy using a patterned Ta capping layer as a catalyst to locally convert CoO/Pd to Co/Pd

and the control pattern are compared in Fig. 4.16. A larger coercivity in the patterned area than the control area is observed, confirming the success of this technique.

4.4.2 Advantages and Limitations

Considerable efforts have been made to achieve nanoscale magnetic structures, such as deposition on prepatterned structures, etching continuous films, and ion irradiation, which have been briefly discussed in *Chapter 1*. Those existing techniques either have issues like edge damage from ion mill process and redeposition on side walls, or experience side effects of change of structure shape after pattern transfer. The newly developed proton irradiation process has not been able to produce high anisotropy media yet. In our study, an innovative

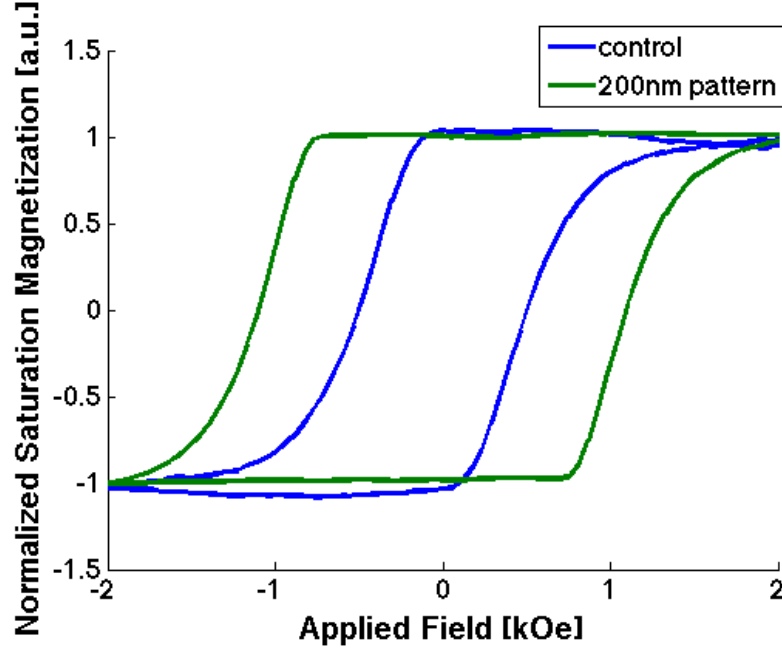


Figure 4.16: Hysteresis loops comparing the switching property of $[\text{Co}/\text{Pd}]_5$ multilayers converted from $[\text{CoO}/\text{Pd}]_5$ multilayers by a $500\ \mu\text{m} \times 500\ \mu\text{m}$ Ta control pattern and a Ta array pattern of 200 nm squares

approach is introduced which includes patterning Ta capping layer instead of patterning magnetic layers directly. This technique can potentially bring significant improvement on the fabrication process and film quality, since Ta can be patterned with good control via RIE and no ion mill is needed in this technique. However, once the size of Ta nano islands, which serve as catalysts in the process, reaches the order of the thickness of thin film ($\sim 5\ \text{nm}$), more close studies regarding diffusion activities of oxygen atoms in CoO layers and the transition from CoO region to Co region are inevitable.

CHAPTER 5 CONCLUSION AND FUTURE WORK

Nonmagnetic CoO thin films and $[\text{CoO}/\text{Pd}]_N$ multilayers have been converted to ferromagnetic Co thin films and $[\text{Co}/\text{Pd}]_N$ multilayers in the presence of Ta gettering layers by low temperature annealing. Magnetic properties of converted thin films and multilayers resemble that of the sputtered magnetic materials. A nanoscale patterning scheme using patterned Ta islands as catalysts for low temperature annealing is proposed and ~ 200 nm $[\text{Co}/\text{Pd}]_N$ nanostructured arrays have been converted using this technique.

This work demonstrates a unique and simple way to make magnetic thin films, multilayers, and nanostructured arrays. In the long term, future work can be focused on:

- Fabricating CoO/Pd multilayers with better magnetic properties (higher anisotropy) after conversion, in order to adapt this technique to useful applications;
- Figuring out the crystal structure of sputtered CoO, if there is one;
- Investigating the size limitation of nanostructured arrays that can be converted;
- Modeling the diffusion of oxygen atoms in the process and compare the results with experiments;
- Performing measurements on Magnetic Force Microscope to seek a visual understanding of magnetic domain structure after conversion;
- Studying the influence of the Ta layer thickness in this process.

Last but not least, it is important to understand that this conversion process can be adapted to other systems where thermodynamically favorable combination of oxide and gettering layers can be identified. Applications that benefit from this study should not be limited to magnetic recording media and potential applications need to be explored in the future for systems where metals and metal oxides are both present in the structure.

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