Chapter 5

NANOSCALE STRUCTURAL AND MAGNETIC CHARACTERIZATION USING ELECTRON MICROSCOPY

David J. Smith and Martha R. McCartney
Department of Physics and Astronomy and Center for Solid State Science
Arizona State University, Tempe AZ 85287-1504, USA

Rafal E. Dunin-Borkowski
Department of Materials Science and Metallurgy
University of Cambridge
Cambridge, CB2 3QZ, United Kingdom

Abstract  The transmission electron microscope (TEM) is a powerful instrument for structural, chemical and magnetic characterization at the nanoscale. Imaging, diffraction and microanalytical information can be combined with complementary micromagnetic information to provide a more thorough understanding of magnetic behavior. The first part of this chapter provides a brief overview of TEM operating modes that are suitable for examination of magnetic materials. The latter part provides examples that serve to illustrate the diverse range of materials that can be usefully studied.

1. INTRODUCTION

Novel physical properties are demonstrated by magnetic materials as their dimensions are reduced towards the nanoscale. Important examples include the giant magnetoresistance (GMR) effect in magnetic/non-magnetic multilayers [1], and oscillatory exchange coupling between magnetic thin films, which depends on the thickness of the non-magnetic spacer layer [2]. Such unique properties of magnetic thin films and nanostructures hold great promise for the development of novel nanoscale storage devices and sensors. However, for successful utilization, it is essential to correlate the magnetic behavior of the materials with their microstructure. In particular, such characteristics as interface roughness, film texture, crystallographic defects, and chemical mixing can have adverse effects on magnetic response. An
understanding of the interdependence between growth and synthesis conditions, microstructure and magnetic properties is essential.

The transmission electron microscope (TEM) enables the local microstructure and magnetic properties of a material to be visualized directly with high spatial resolution, unlike bulk techniques such as X-ray diffraction and Rutherford backscattering. Technical advances in the high-resolution electron microscope (HREM) have resulted in performance improvements that enable atomic-scale detail to be resolved on a routine basis [3]. A range of imaging, diffraction and microanalytical modes is readily available in modern TEMs, and can be used to obtain this essential nanoscale information. Imaging techniques include transmission and high-resolution electron microscopy and Z-contrast annular-dark-field imaging, while nanospectroscopy approaches include electron-energy-loss and energy-dispersive X-ray spectroscopy as well as energy-filtered imaging. The TEM can also be used to provide micromagnetic information about materials over a wide range of length scales with a spatial resolution that cannot be approached by most other instruments. TEM methods that are specifically used to highlight micromagnetic features include Lorentz microscopy [4] and electron holography [5]. We begin this chapter with a brief introduction to these various imaging, nanospectroscopy and micromagnetic operating modes. We then describe in more detail some representative applications of these techniques to the characterization of nanostructured magnetic materials.

2. ELECTRON MICROSCOPY METHODS

In the transmission electron microscope, the finely focused electron beam, with a wavelength typically of much less than 0.1nm, is used to form a highly magnified image of the specimen region of interest. The conventional transmission electron microscope (CTEM) uses a broad circular beam with a diameter of about 0.5-1.0 microns, which is transmitted through a suitably thinned specimen. In the scanning transmission electron microscope (STEM), a focused nanoprobe is rastered across the sample. The transmitted electrons are then used to form a modulated image on a display monitor that is synchronized with the incident scan. CTEM images have historically been recorded on photographic film, but digital recording with charge-coupled-device (CCD) cameras enables quantitative analysis, and has become widespread. Unavoidable electron lens aberrations normally restrict image resolutions to the 0.25-0.1 nm range for electron energies of 200-1250 keV. Nevertheless, atomic arrangements can be resolved in many different inorganic materials when they are imaged in low-index crystallographic orientations. When the nanoprobe of a STEM is stopped at specific sample
locations, the detection of characteristic X-rays emitted by the sample or the examination of the energy-loss spectrum of the transmitted electrons enables element-specific information to be obtained. These microanalytical signals can be used to provide highly useful complementary information about local defects or inhomogeneities in magnetic materials which may in turn influence or even determine their magnetic behavior.

2.1. Transmission Electron Microscopy

In the standard operating mode of the TEM, usually referred as amplitude or diffraction contrast imaging, electrons that have been transmitted by the sample are used to form a highly magnified image of the specimen feature of interest on a final viewing screen or recording medium. A small objective aperture is typically used to prevent most of the scattered (or diffracted) electrons from reaching the final image plane, in order to determine the image contrast. Crystalline samples are usually aligned by reference to their electron diffraction pattern (EDP) to ensure that the specimen orientation relative to the incident electron beam direction satisfies a strongly diffracting condition. Under such conditions, many common types of defects then have a highly characteristic appearance, potentially allowing identification of any second-phase materials. Crystal lattice spacings and the angles between lattice planes can also be measured and determined by reference to the EDP. The availability of a crystalline substrate or supporting medium often provides a useful method for orientation of the sample in the electron microscope. By using the substrate EDP as a reference, it becomes possible to align an internal interface of interest so that it is perpendicular to the electron beam direction. Changes in the microstructure of thin films and multilayers, either laterally or as a function of distance from the substrate can then be determined. As an example, Fig. 1 shows several diffraction contrast images of thin CoFe films grown directly on the native oxide of a Si substrate at room temperature and at 100°C, and also grown on a CoO buffer layer [6]. Considerable changes in the morphologies of the CoFe thin films, including the average widths of the columnar grains, result from the differences in the growth conditions. These changes could be correlated with marked changes in the measured coercivities of the different films. Finally, it should be appreciated here that the examination of complex multilayered samples can represent a serious challenge to the electron microscopist because it can be often difficult to prepare typical regions that are electron-transparent across the entire region of interest simultaneously. Different approaches for preparing electron-transparent specimens that have been developed, and are described in some detail below.
2.2. High-resolution electron microscopy

In high-resolution or phase-contrast imaging, a large objective aperture (or sometimes no aperture at all) is used. One or more diffracted beams interfere with the directly transmitted beam to form the image, and the image contrast then depends on the relative phases of the various beams. This mode of operation can thus be termed phase-contrast imaging. When the imaging conditions (correct lens defocus, no image astigmatism, accurate incident beam alignment) are properly optimized, phase-contrast images can be directly interpreted in terms of the projected crystal potential. In recent generations of TEMs, the image resolution is usually better than 0.2 nm, so that individual atomic columns can be resolved in many crystalline inorganic materials. For direct image interpretation with the highest possible spatial resolution, the specimen thickness must be less than about 10 nm. High electron doses, typically ~ 500-2000 electrons per square Ångstrom, are required to record such images, which means that specimens for high-

Figure 1. Cross-section diffraction contrast electron micrographs showing changes in morphology of 30-nm CoFe thin films depending on specific growth conditions: (a) grown at room temperature on Si substrate; (b) grown at 100°C on Si substrate; (c) grown at 100°C on CoO (10 nm) intermediary layer [6].
resolution studies must be relatively resistant to electron irradiation effects. It is impossible to examine most organic materials and polymers directly under such intense imaging conditions. By using a specimen heating holder, and by adding a TV-rate image-pickup system to the base of the electron microscope lens column, dynamic events can be followed in real time without significant loss of spatial resolution.

Over the past 40 years, the technique of high-resolution electron microscopy has been used to characterize a wide range of inorganic materials. Important applications include determining the detailed microstructure of defects, interfaces and grain boundaries, investigating nanocrystalline features in amorphous films, and studying small particles in heterogeneous catalysts. The characterization of magnetic thin films and multilayers continues to be very important, since layer continuity and defect microstructure are crucial to the viability of recording media. High-resolution images are able to provide site-specific details that are usually unavailable using other techniques. As an example, Figs. 2(a) and (b) show two high-resolution electron micrographs that illustrate the amorphous or polycrystalline nature of the barrier layers in simple magnetic tunnel junctions (MTJs) grown by dc reactive sputtering [7]. The layer sequences in the images are: (a) Co (50nm)/ HfO$_2$ (10nm)/Fe (50nm), and (b) Co (50nm)/ CoO (10nm)/Fe (50nm).

Figure 2. (a) High-resolution electron micrograph of Co(50 nm) / HfO$_2$ (10 nm) / Fe(50 nm) tunnel junction showing amorphous nature of barrier layer; (b) Cross-sectional electron micrograph of Co/CoO/Fe tunnel junction showing polycrystallinity prevailing in CoO barrier layer [7].
### 2.3. Nanospectroscopy

Many modern electron microscopes are equipped with high-brightness field-emission-gun electron sources which are able to provide a small, high intensity electron probe at the level of the specimen. Such nanoprobes allow complementary chemical information to be obtained from sub-nanometer-sized regions. Specimens that are intended for microanalysis must be thin (< 50 - 100 nm) in order to avoid multiple scattering effects that would lead to loss of spectral resolution and sensitivity. Their surfaces must be carefully cleaned if quantitative analysis is to be performed since substantial carbon contamination may otherwise occur during small-probe observations. It is thus becoming common-place to clean both the TEM sample, and the sample holder, in a plasma-cleaning device immediately prior to insertion in the electron microscope. Moreover, it must be appreciated that an intense stationary electron probe can itself alter the local microstructure and composition of a sample significantly.

The technique of electron-energy-loss spectroscopy (EELS) is used to measure the energy-loss spectrum of electrons that have been transmitted

![Figure 3](image.png)

**Figure 3.** (a) Annular-dark-field electron micrograph of [Fe (2 nm)/ oxide]₅₀ showing path of EELS probe; (b) O/Fe ratio along line scan for model profile (solid curve), convolved profile (dotted curve) and experimental points (filled circles) [8].
through a specimen. The EELS spectrum consists of a monotonically decreasing background and a series of peaks, which typically have characteristic energies in the range of 100 to several thousand eV, which are directly related to inelastic scattering processes that are specific to the elements in the specimen. Information can thus be obtained from an EELS spectrum about elemental composition, as well as about chemical bonding and electronic structure. The spatial resolution of this information is determined primarily by the focused probe diameter, provided that the specimen is not too thick. Quantification of elemental composition can attain sensitivity levels approaching better than one atomic percent. EELS can also be used to measure changes in near-edge fine structure, enabling oxidation states to be determined. EELS can be applied to magnetic materials when chemical information about interfacial abruptness is needed, for example after multilayer deposition or after extended annealing cycles. Diffusion profiles across interfaces can then be extracted from EELS data, provided that the effects of the finite probe size on the elemental profiles are properly taken into account. An interesting example of an [Fe(2nm)/oxide]_{50} multilayer structure is shown in Fig. 3. In this study [8], convolution of the expected composition (solid line) with an appropriate probe function gave a convoluted profile (dotted line) that was in close agreement with the experimental points (filled circles), indicating unexpectedly that the Fe:O stoichiometry of the native oxide was close to unity.

The technique of energy-dispersive X-ray spectroscopy (EDXS) utilizes the characteristic spectrum of X-rays that is emitted by a sample following initial excitation of an inner-shell electron by the high-energy electron beam to a vacant higher-energy level. Highly localized information about the elemental composition of the sample can again be obtained, with the spatial resolution determined primarily by the probe size and by any beam broadening that has occurred within the specimen. EDXS is a relatively straightforward technique experimentally, and it can be used to provide rapid qualitative microanalysis. Quantitative elemental analysis can also be achieved, with an accuracy that can approach a few atomic percent. However, thin specimens are required for quantitative EDXS analysis because of the need to avoid spurious signals arising from any backscattered electrons. Moreover, (pre-)calibration of the specific EDXS analysis system using standards of known composition is necessary. EDXS is better suited than EELS for detecting elements of high atomic number (Z). However unlike EELS, it is unable at present to provide any information about local bonding. Low-Z elements (Z < 11) are not detectable by some EDXS systems due to absorption by the detector window, but this shortcoming can be overcome by using ultrathin or even window-less detectors. Care is required when performing EDXS analysis because of the possibility of
detecting X-rays originating from the microscope column or from regions of the specimen away from the area of interest.

2.4. Energy-filtered imaging

Energy-filtered imaging is a TEM technique based on EELS that allows information about the spatial distribution of elements in a sample to be obtained. By using an energy-selecting imaging spectrometer, located either in the post-specimen lens column or below the final viewing screen, only those electrons that have lost energies within a specific energy range are used to form the final image. Since electrons in the low-loss energy region of the spectrum (plasmon or valence-loss electrons) are not very sensitive to variations in composition, those originating from characteristic inner-shell ionization edges are instead normally used for image formation. The selection of electrons for imaging is accomplished by using an energy-selecting slit of variable width, and some sort of background subtraction.

![Figure 4](image_url)

Figure 4. Energy-filtered image of Cr-doped GaN showing considerable Cr clustering. Inset above shows Cr EELS line profile [9].
routine is required in order to separate the desired element-specific contributions from the background signal. Although the quality and spatial resolution of energy-filtered images suffer from poor signal-to-noise due to low inelastic scattering cross-sections, elemental mapping provides a highly useful technique for extracting valuable compositional information about magnetic materials. As an example, Fig. 4 shows an energy-filtered image of a cross-sectioned Cr-doped GaN epilayer, as grown by reactive molecular-beam epitaxy at 825°C, under investigation for possible ‘spintronic’ applications [9]. Unlike companion samples grown at lower temperatures which had relatively uniform Cr doping, this specimen showed considerable Cr clustering, which was believed to account for its lower coercivity when compared with the other samples.

2.5. Lorentz microscopy

The magnetic microstructure of a TEM specimen is not normally visible under conventional operating conditions. In particular, the strong magnetic field (~2T) at the specimen level generated by the objective lens modifies or even completely destroys any intrinsic magnetic domain structure inside a TEM specimen. Such severe restrictions for studying magnetic materials using the TEM have led to the development of several alternative imaging modes. These are collectively known as Lorentz microscopy, since they are based on the sideways deflection of the charged high-energy electron inside a magnetic specimen by the Lorentz force. Since the objective lens is usually switched off for Lorentz imaging, the spatial resolution of the magnetic detail revealed in Lorentz micrographs is substantially degraded when compared with conventional imaging. However, this loss of resolution is not normally considered as a serious obstacle since magnetic fields only rarely change abruptly on a sub-nanometer scale.

The simplest and most common technique for imaging magnetic domain structures is the so-called Fresnel or defocus mode of Lorentz microscopy. Electrons traversing domains with different magnetization orientations are deflected in different directions, creating regions that have either an excess or a deficit of electrons immediately below the sample. By imaging in an under- or over-focus condition, lines of black or white contrast appear at the positions of the domains walls. This configuration is illustrated schematically in Fig. 5(a), and an example of a Lorentz micrograph taken in the plan-view geometry from a CoPtCr /alumina /Co MTJ is shown in Fig. 5 (b) [10]. By measuring the apparent domain-wall width as a function of (pre-calibrated) defocus, a quantitative estimate of the wall width can be extracted. The alternative Foucault mode of Lorentz microscopy involves the use of a small objective aperture to select for imaging only those electrons that have been deflected in a specific direction. The image contrast of
Foucault images is highly sensitive to aperture position, and quantitative information is virtually unobtainable. However, domain configurations are easily recognized using this approach. Despite inherent spatial resolution limitations of Fresnel or Foucault imaging, either technique allows useful real-time viewing of dynamic processes.

Figure 5. (a) Schematic of Lorentz imaging; (b) Lorentz micrograph from CoPtCr (15 nm)/ alumina /Co (10 nm) magnetic tunnel junction during field-cycling. Domain walls and ripple contrast due primarily to the soft Co layer [10].
2.6. Electron holography

The technique of electron holography permits retrieval and quantification of both the amplitude and the phase shift of the electron beam that has traversed through a TEM specimen, unlike the situation for normal imaging where all phase information is lost [5]. Since the phase shift of the electron which has passed through the sample can be directly related to magnetic (and electric) fields, electron holography provides a powerful way to probe magnetic microstructure. There are many types of electron holography, but the mode known as off-axis or sideband electron holography, as illustrated in Fig. 6, is most commonly used. A field-emission electron gun is used to provide a coherent source of electrons. A thin, positively charged wire (or ‘biprism’) is then used to provide interference between the reference wave that has passed through vacuum and the object wave that has passed through the specimen. The biprism is usually located in the selected-area aperture plane of the microscope below the sample. Historically, photographic film was used for recording holograms but it has recently become commonplace to record the final holographic interference pattern using a CCD camera. Digital recording greatly benefits the process of hologram reconstruction and phase quantification. Once the phase shift of the electron wave has been

![Electron Holography Diagram]

Figure 6. (Left) Schematic showing basic TEM configuration for off-axis electron holography; (Right) Photograph showing electron microscope suitably equipped for recording holograms of magnetic materials.
reconstructed, quantitative information with high spatial resolution about the magnetic (and electric) fields in a sample can be easily extracted. The convenient availability of the so-called ‘Lorentz minilens’ just below the sample enables moderate magnifications (~50,000x) to be achieved during observation of magnetic materials with the normal objective lens completely switched off and with the sample located in a magnetic-field-free condition. Alternatively, a weak vertical field can be achieved by slightly exciting the objective lens, thus enabling in-plane magnetic fields to be applied in situ by tilting the sample. Hysteresis loop response of FM nanostructures can be determined directly, as shown later in Section 3.5.

3. NANOSTRUCTURED MAGNETIC MATERIALS

Many different types of nanostructured magnetic specimens are of interest, with a host of possible applications. For example, a sample may consist of granular or polycrystalline magnetic thin films or multilayers, complicated structures such as exchange-biased magnetic tunnel junctions or magnetic tunneling transistors, or it may contain nanoscale patterned features. It can sometimes be a serious drawback of TEM methods that thin sections of a material are required for examination. Since the micromagnetic features usually extend into at least two, and more usually three, dimensions, specimens for observation must often be prepared in two or even three orthogonal directions, i.e. in both plan-view and cross-sectional geometries. Plan-view specimens can be straightforward to prepare using methods such as chemical etching or mechanical polishing. In other cases, mechanical polishing and dimple-grinding are required, followed by ion-beam milling at low beam energies. This latter approach will generally lead to larger regions of thinned material. The preparation of suitable cross-sections sometimes necessitates the use of costly ancillary equipment such as a focused-ion-beam system, and it can be time-consuming and tedious to achieve thin specimen areas that are genuinely representative.

The cross-sectional viewing geometry is necessary when the features of interest are buried within the material or else distributed throughout the depth of the sample because of its layered structure. The planarity of buried interfaces can be determined, and the distribution, width and composition of interfacial defects and the presence of any secondary phases such as pinholes across tunnel junctions can be assessed. Cross-sectional specimens are typically prepared by glueing the material of interest face-to-face onto additional supporting material. Mechanical polishing of a thin slice of this stack, followed by dimple-grinding, is used to reduce the total overall thickness to ~5-10 microns. Final milling with an argon-ion-beam is used to achieve perforation of the cross-sectional film. Thin areas of the interface are
created where the perforated hole intersects the glued faces. The damage to some magnetic materials that occurs during cross-sectional specimen preparation can be reduced by ion-milling with the specimen held at liquid nitrogen temperature. Specimens that contain materials with very different ion-milling rates, such as metallic multilayers grown on silicon substrates, often tend to form bridges of material across the perforated area. Ion-milling at very low angles of incidence (~1-2°) in a direction parallel to the interface can sometimes be used to overcome or at least alleviate these bridging problems. Finally, it should be noted that the use of a crystalline substrate such as silicon provides a convenient reference material for specimen orientation purposes in the TEM. Examination of the substrate EDP can be used to ensure that the substrate normal is aligned exactly perpendicular to the electron beam direction. The thin-film microstructure can then be easily determined.

3.1 Thin films and multilayers

Figure 7. (a) High-resolution image showing part of (111)-oriented Cu(0.9 nm)/Co(1.0 nm) GMR multilayer. (b) Defocused low-magnification image of Cu/Co multilayer showing clear delineation of separate Cu and Co layers [12].
Magnetic thin films and multilayers are typically prepared by sputtering or molecular beam epitaxy (MBE), often using computer control of deposition parameters to ensure high reproducibility. Single crystal Si with various surface normals, and sometimes GaAs or MgO, are commonly used as substrates for growth. MBE facilitates epitaxial growth of high quality crystalline samples. Any orientation dependence of the magnetic behavior can then be investigated by choosing suitable substrates that induce the films to grow in specific orientations. In contrast, sputtering generally provides polycrystalline films and permits greater sample throughput, allowing trends in behavior with changes in deposition parameters to be correlated rapidly and systematically. Indeed, sputtering was used in early studies of polycrystalline Co/Cu multilayers that exhibited GMR values as high as 65% at room temperature and 115% at 4.2 K [11]. Later studies showed that highly-oriented (111), (110) and (100) Co/Cu superlattices of excellent crystallinity could be grown by sputtering onto substrates of sapphire, MgO (110) or MgO (100), respectively, and using thin (~1.2-1.5nm), intermediary seed layers of Pt or Pd [12]. Figure 7(a) shows part of a {111}-oriented [Co (1.0nm)/Cu (0.9nm)]_{24} superlattice. Strong, two-dimensional {111} lattice fringes are visible, revealing considerable structural disorder, including stacking faults and twins, although the individual layers cannot be seen. In order to highlight the anticipated compositional contrast from the individual Co and Cu layers, it was necessary to record defocused diffraction contrast images with a small objective aperture, as shown in Fig. 7(b).

Crystalline FePt thin films are of much interest because of the possibility of forming the chemically ordered L1_0 tetragonal phase, which has very high magnetocrystalline anisotropy. Figure 8 shows an example of a

![Figure 8](image_url)  
Figure 8. High-resolution electron micrographs showing cross-section of FePt/Pt/MgO sample: (a) [001] projection. Note surface flatness; (b) [110] projection showing FePt/Pt/MgO interface region. Insets show corresponding selected-area electron diffraction patterns [13].
high quality, epitaxial Fe\textsubscript{x}Pt\textsubscript{1-x} (x \approx 0.6) film grown by MBE on an MgO substrate held at 300°C during deposition \cite{13}. The use of a thin (~1.5nm) Pt seed layer in this case was found to be necessary in order to establish the desired single growth orientation of the alloy film. Doubling of the \{200\} lattice-fringe period was observed along the horizontal direction of this sample (surface normal vertical), indicative of the desired compositional modulation. Further TEM observations of films grown at 500°C established the presence of more extensive ordered regions, consistent with the much larger short-range-order parameter (S = 0.81) relative to that obtained for growth at 300°C (where S = 0.39).

3.2. Tunnel junctions and spin-tunneling transistors

Spin-dependent magnetic tunnel junctions (MTJs), which consist of two thin ferromagnets (FMs) separated by a narrow insulating barrier, display large conductance changes when the relative magnetization alignments of the FM layers are reversed. Devices based on this alignment effect, such as magnetic random access memory (MRAM), utilize the large MR difference between the parallel/anti-parallel configurations for sensing and recording purposes. Two basic types of MTJ have been developed. The simplest consists of two FM materials that have different switching fields, usually referred to as ‘hard’ – ‘soft’. A more complex MTJ structure has an additional antiferromagnetic layer adjacent to one of the FM layers, which has the effect of exchange-biasing or ‘pinning’ the magnetic moment of this particular layer so that its hysteresis loop is offset sideways from zero field by the exchange field. In both of these MTJ geometries, successful device fabrication and operation depends on several factors, including the uniformity, stoichiometry, and thermodynamic stability of the insulating

\[ \text{CoPt} \]
\[ \text{Al}_2\text{O}_3 \]
\[ \text{CoPtCr} \]
\[ \text{CrV} \]

\[ \text{CoPt} \]
\[ \text{Al}_2\text{O}_3 \]
\[ \text{CoPtCr} \]

**Figure 9.** (a) Cross-section of simple MTJ before annealing; (b) High-resolution image of barrier region after annealing at 350°C \cite{14}.
layer, and the quality (smoothness and compositional abruptness) of the FM-insulator interfaces.

Figure 9 shows an example of the simpler type of MTJ structure [14]. The micrograph in Fig. 9(a) displays the entire cross-section of an MTJ consisting of magnetically hard Co$_{75}$Pt$_{12}$Cr$_{13}$ (15 nm)/ alumina barrier (~2.5 nm)/ magnetically soft Co$_{88}$Pt$_{12}$ (15 nm), with an underlying layer of Cr-V which is used here as a seed layer to promote growth of the hcp Co-Pt-Cr alloy with its easy (or c) axis in the plane of the film. Figure 9(b) is a high-resolution electron micrograph showing the barrier region after annealing at 350°C. Extensive observations of annealed MTJs have been used to show that the alumina layers remained continuous and relatively flat after annealing, although the mean barrier thickness decreases slightly from 2.7 nm for the as-grown samples to about 2.5 nm after annealing.

![Figure 9(a)](image1.png)

**Figure 9.** Cross-sectional electron micrographs of possible Ru-based magnetic tunneling transistor. (a) low magnification image, also showing antiferromagnetic IrMn layer; (b) high-magnification image showing central barrier and Ru layer interaction with Si substrate [15].
Much attention has recently been directed to ‘spin-tronic’ devices, which aim to utilize the spins of the conduction electrons as well as their charge for very high density information storage purposes. The magnetic tunneling transistor (MTT), which is based on an exchange-biased MTJ of the second type described above, has emerged as a possible candidate for providing highly efficient spin injection. The core of the MTT consists of an FM emitter, a tunnel barrier, an FM base, and a final semiconductor collector. Since spin-polarized electrons must overcome a Schottky barrier at the base/collector interface, the use of thin intermediary seed layers represents a possible mechanism for enhancing device sensitivity. Figure 10 (a) shows a cross-sectional electron micrograph of a possible Ru-based MTT. The enlargement in Fig. 10(b) shows the region near the Ru seed layer in greater detail [15]. Some interdiffusion or reaction with the Si substrate, also confirmed by small-probe microanalysis, has taken place, and could account for the low junction breakdown voltages measured for the Ru-based MTT devices.

3.3. Discontinuous multilayers and metal-insulator granular films

![Discontinuous magnetic layers](image)

**Figure 11.** Discontinuous magnetic layers: a) plan-view of single layer - SiO₂(3 nm) /Co(2 nm) /SiO₂(3 nm); b) cross-section of Co/SiO₂/Co DMTJ [16].
Discontinuous multilayers, which consist of planes of metallic FM particles interspersed within an insulating matrix are easy to prepare, and they offer several distinct advantages over continuous magnetic layers and especially MTJs. The benefits include less susceptibility to electrical breakdown and greatly reduced likelihood of pinhole development across the insulating barrier, which often serve to short-circuit the current in a regular MTJ structure. Figure 11(a) shows a plan-view image of a simple trilayer system consisting of SiO$_2$ (3nm)/Co (2nm)/SiO$_2$ (3nm) [16]. In this case, the Co particles (dark contrast) form short chains of clusters of 3.5-nm approximate width. It is clear that the layer is indeed discontinuous. Figure 11(b) shows a cross-section electron micrograph of a discontinuous magnetic tunnel junction (DMTJ), consisting of two planes of magnetic Co nanoparticles sandwiched between three insulating SiO$_2$ layers. After moderate annealing, this simple bilayer DMTJ showed an MR of ~4% at room temperature. Annealing (300-350°C) of similar multilayers consisting of 20 bilayers, led to increased numbers of superlattice (SL) reflections visible in electron diffraction patterns, suggesting some sharpening of the metal/insulator interfaces, whereas over-annealing (≥ 400°C) led to a decrease in the number of SL reflections implying deterioration of the interfaces, most likely due to interdiffusion or possibly metal oxidation.

Granular films, rather than multilayers, which consist of FM nanoparticles dispersed within a non-magnetic insulating matrix, display interesting spin-dependent transport behavior that is determined primarily by particle size. Electron micrographs from co-deposited Co-SiO$_2$ granular films, such as the example shown in Fig. 12, confirmed that the films basically consisted of small hcp Co particles distributed relatively uniformly throughout the SiO$_2$ matrix [17]. Further TEM observations as a function of increasing Co volume fraction up to percolation gave good agreement with estimates of particle size based on magnetic susceptibility measurements.

**Figure 12.** Electron micrograph showing co-deposited Co-SiO$_2$ granular film containing approximately 32 vol.% Co [17].
3.4. Nanostructures

Characterization of the micromagnetic states of FM nanostructures using off-axis electron holography becomes increasingly challenging when their dimensions are reduced below 100 nm, primarily as a result of a fundamental signal-to-noise limit on the detection of small phase gradients, rather than the available instrumental spatial resolution. Nevertheless, recent results demonstrate the feasibility of studying the magnetization behavior of closely-spaced nanoparticles and nanowires that have one or more dimension in the 5 - 100 nm range. As an example, Figures 13 (a) and (b) show the magnetic remanent states of several Fe\textsubscript{0.56}Ni\textsubscript{0.44} nanoparticle chains, as determined by electron holography [18]. Interpretation of the phase contours suggests the presence of magnetic vortex states surrounding a central flux channel, as drawn schematically in Figs. 13 (c) and (d). The unexpected complexity of these observations, which was confirmed by extensive micromagnetic simulations, reinforces the need to understand and control the effects of size, shape and proximity of magnetic nanoparticles intended for potential storage applications.

![Figure 13](image_url)

**Figure 13.** (a) and (b) Experimental magnetic phase contours showing the strength of the local induction (integrated in the electron beam direction) in two different chains of Fe\textsubscript{0.56}Ni\textsubscript{0.44} particles. (c) and (d) show schematic representations of the magnetic microstructure in the chains. Magnetic vortices spinning about the chain axis are visible in (c) and (d). A vortex spinning perpendicular to the chain axis is also visible in (d). [18].
Another intriguing example of magnetostatic interactions between closely-coupled nanoparticles is illustrated in Fig. 14 [19]. This study involved Co nanoparticles, with diameters in the range of 20 - 30 nm, which had spontaneously formed rings, chains and other close-packed aggregates. Examination by electron holography established the existence of flux closure remanent states associated with each cyclic ring ensemble, having either clockwise or counterclockwise configurations, as shown in Figs. 14 (b) and (c).

![Image of Co nanoparticles](image)

**Figure 14.** (a) Low magnification bright-field image of self-assembled Co nanoparticle rings and chains deposited onto an amorphous carbon support film. Each Co particle has a diameter of between 20 and 30 nm. (b) and (c) Magnetic phase contours (128 × amplification; 0.049 radian spacing), formed from the magnetic contribution to the measured phase shift, in two different nanoparticle rings. The outlines of the nanoparticles are marked in white, while the direction of the measured magnetic induction is indicated using arrows [19].
3.5. Patterned nanostructures

For a fuller understanding of nanoparticle interactions and magnetic response, it is desirable to have better control over particle placement and geometry. Moreover, stable and reproducible magnetization states are essential for potential device applications. Patterned of FM nanostructures enables systematic electron-holographic studies of remanent states and magnetization reversal processes to be made as a function of element size, thickness and shape. Magnetostatic interactions between closely separated particles can also be investigated. The left part of Fig. 15 shows some representative results of reconstructed holograms from two 30-nm-thick rectangular Co elements (275x220 and 275x300 nm, separated by 170 nm).

Figure 15. (a) Magnetic contributions to measured phase shifts of holograms of 30-nm-thick Co rectangular elements for entire magnetization reversal cycle, for applied in-plane fields indicated. Contour spacing of 0.21π radians. The images should be followed in a counterclockwise sense [20]. (b) Best-fitting micromagnetic simulations to hysteresis cycle shown in (a). Initial states in the top image are an S-state for the smaller rectangle and a C-state for the larger rectangle [21].
over an entire hysteresis cycle [20]. The occurrence of solenoidal (or vortex) states at close to zero in-plane fields for both directions of the cycle coincides with minimal fringing fields between the elements. Further work using micromagnetic simulations, as shown in the right hand panel, revealed that the close proximity of the neighboring cells had assisted in trapping these domain states [21]. The lack of reproducibility of particular domain structures during magnetization cycles for some elements, which is of obvious importance for device applications, was noted in this study. The formation of vortex states during switching is also undesirable from an applications point of view because they usually persist to much greater switching fields.

Recent attention has been directed towards circular magnetization modes (i.e., clockwise and counterclockwise), rather than linear modes as an alternative basis for storage logic [22]. However, variability and reproducibility of reversal processes for nanoscale disk-shaped elements are likely to be a serious issue, prompting consideration of modified shapes such as rings, as well as slotted disks and slotted rings. Ring-shaped elements have switching behavior that varies significantly depending on the ratio of the outer-ring/inner-ring diameters [23]. Reversal proceeds either via a

---

**Figure 16.** Amplified (8x) phase images of 400 nm/50 nm Co ring during entire hysteresis cycle. In-plane field magnitude indicated below each image (units of Oe). Note vortex states visible in (d), (e) and (j), (k). From [23].
coherent domain-wall rotation or via the formation of an intermediate vortex state, as shown by the example in Fig. 16. Interestingly, these vortex states were not observed to occur in any remanent states of the rings..

3.6. Minerals and biogenic crystals

Closely spaced magnetic nanocrystals that are found in nature are often more perfect in their sizes, shapes and arrangements than their synthetic counterparts. As a result, they can be chosen as model systems to study the effect of particle size, morphology, crystallography and spacing on magnetic microstructure. Figures 17(a) and (b) show chemical maps of a crystalline region of a naturally occurring magnetite-ulvöspinel (Fe₃O₄-Fe₂TiO₄) mineral, which has exsolved during slow cooling to yield a three-dimensional intergrowth of ferrimagnetic magnetite-rich blocks that are separated by non-magnetic ulvöspinel-rich lamellae [24]. Figures 17(c) and
(d) show two remanent magnetic states recorded from the same region using off-axis electron holography. The domain structure in the images is extremely complex, and a saturated domain structure was never observed at remanance. The abundance of single domain states implies that they have a lower energy than vortex states in the presence of strong interactions with neighboring magnetic crystals. Similar magnetic interactions have been observed in linear chains of ferrimagnetic magnetite crystals in magnetotactic bacteria, which are oriented passively in the direction of the earth's magnetic field in aquatic environments [25]. A magnetic induction map recorded from a single helical bacterial cell containing a chain of equidimensional magnetite crystals is shown in Fig. 18. The magnetic phase contours are highly constrained to be parallel to each other within the crystals and to follow the chain axis. Unlike the more complicated magnetic arrangement seen in Fig. 17, the magnetic moment in the linear bacterial chain is maximized, and its remanent magnetic state is almost equivalent to its saturated state.
4. CONCLUDING REMARKS

The examples described in this chapter have been carefully chosen to
demonstrate the broad diversity of information about magnetic thin films and
nanostructures that becomes available from examination in the electron
microscope. The powerful combination of microstructural, microanalytical
and micromagnetic information at the nanoscale facilitates a more detailed
understanding of basic magnetic properties. Current resolution levels for
imaging and microanalysis are more than adequate, but future micromagnetic studies would benefit from enhancement in the strength of
the available magnetic signals. The combination of electron holography
with electron tomography could also enable the determination of three-
dimensional magnetic vector fields in and surrounding nanoscale objects.

ACKNOWLEDGMENTS

We are pleased to acknowledge friends and colleagues for their involvement
in the work described here. Many of these studies involved use of the facilities in the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

REFERENCES

Nanoscience and Nanotechnology”, Ed. H.S. Nalwa, American Scientific, Stevenson
Ranch 2003, Volume 3, pp. 41-100.
(2000).