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Status of Effort

The fourth reporting period was a most productive one, with the MURI team producing work with significant impact to the spintronics and magnetic materials science and technology base. Some of the highlights include:

(i) fabrication of Ni nanowires by different methods and a comparative study of their properties.
(ii) use of CoFeB amorphous layers in spin-valves.
(iii) CO/NH$_3$ non-corrosive etching of magnetic materials.
(iv) long-term stability study of dry-etched magnetic elements.
(v) size-effects in magnetic and superconducting materials.
(vi) study of vortex matching in magnetic structures.
(vii) modelling of display materials.
(viii) PLD of CMR oxides.
(ix) advanced nanofabrication techniques for wires and MRAM elements.
(x) advanced cantilevers for EFM.
(xi) ion beam deposition of GMR materials.
(xii) nanoscale tribology.
(xiii) proximity effects and length scales of magnetism.
(xiv) nanometer Fe particle arrays.
(xv) theory of GMR in different geometries.
1. **Fabrication and Magneto-Transport and SQUID Measurements of Sub-Micron Spin-Valve Structures**

   *(Y.D. Park and D. Temple)*

Sub-micron Ni$_{0.8}$Fe$_{0.2}$/Cu/Co spin-valves and Co/Cu pseudo spin-valves with widths ranging from 200 $\mu$m to 0.5 $\mu$m have been realized by direct deposition and lift-off. The resulting configurations were structurally characterized by atomic force microscope and cross-sectional transmission electron microscopy. Transport and magnetic properties of arrays of these spin-valve structures were studied using superconducting quantum interference device magnetometer. Magnetic measurements carried out on several spin-valve structures showed that both coercivity and field at which maximum magnetoresistance (MR) occurs increase with decrease in widths of the spin-valves. Comparison of the results obtained from the magnetometry and transport measurements indicated the existence of an offset between the coercive field and field of maximum MR. Resistance versus temperature measurements for varying linewidth show a minimal shift in peak temperature, indicating that processing effects are minimal.

Considerable advances in understanding and processing of magnetic thin films have led to rapid development of giant magnetoresistance (GMR) elements for various applications. In a number of these applications sub-micron feature sizes are required to maintain the progress in bit storage density in read/write heads and magnetic random access memory (MRAM). Direct deposition and lift-off have been utilized to realize element dimensions less than 100 nm using e-beam lithography techniques. Characterization of GMR elements is mainly limited to transport measurements by which magnetic properties can be indirectly inferred. Therefore, there are only a limited number of reports about
characterization of magnetic properties using sensitive magnetization techniques such as vibrating sample magnetometer (VSM), superconducting quantum interference device (SQUID) magnetometer, and magneto-optical Kerr effect (MOKE) all of which usually require repeated arrays of GMR elements. In this paper, we report the fabrication of GMR magnetic elements with feature sizes as small as 0.5 µm, using a combination of direct deposition and a lift-off processing techniques and their subsequent characterization by direct magnetization and transport measurements using radiofrequency (rf) SQUID. Direct magnetization measurements by rf-SQUID magnetometer has been correlated with magneto-transport measurements for various magnetic multilayer structures. An advantage of measuring absolute $M_S$ values is a direct comparison and observation of effects, if any, due to processing. These effects are considered extremely important in determining the feasibility of new generations of magnetic devices.

Ni$_{0.8}$Fe$_{0.2}$/Cu/Co and Co/Cu films were deposited directly onto silicon substrates with 1000 Å SiO$_2$ layer and already developed and patterned resist. Direct deposition included both evaporation and ultra-high vacuum (UHV) magnetron sputtering. Further processing steps were conducted near room temperature to prevent degradation of the underlying resist before lift-off. For samples prepared via sputtering, optimal background gas pressure was experimentally determined to minimize shadowing effects at the smallest linewidth.

After deposition of GMR elements, the samples were immersed in commercial resist stripper in an ultrasonic bath at the elevated temperature of 50℃ for up to 15 minutes. The samples were then rinsed in isopropyl alcohol (IPA) and de-ionized water (DI H$_2$O). The patterned elements included sixteen arrays of widths ranging from 0.5 µm to 20 µm with length of 500 µm. These 0.5x0.5 mm$^2$ arrays were used for transport measurements with
each array having geometrical constraint: (number of lines)x(linewidth)+(number of lines – 1)x(space widths) = 0.5mm with linewidth: spacewidth of 1:2. Due to limited design space on the reticle, number of samples for SQUID magnetization measurements (size of 2.5 mm x 6.5 mm) were limited to sample widths of 0.5, 0.8, 1.2, and 2.2 µm, again with lengths of 500 µm and linewidth:spacewidth of 1:2.

For transport measurements, the samples were further prepared to fashion electrical leads and contacts. Leads and contacts were defined by photolithography. The resist was baked on a hot plate at 120° C for 60 seconds to minimize underlying structures longer exposures at elevated temperatures. After development and rinse, four Au/Ge contact pads were thermally evaporated, and lifted-off in acetone bath followed by rinse in IPA and DI H₂O. Each lead spanned the array perpendicular to the elements, yielding a parallel structure. Measurements were conducted using Quantum Design PPMS with an AC bridge. The injected currents were limited to 0.1 mA for all linewidths and typical total resistance of array range of 100 Ω. Magnetoresistance (MR) measurements were generally conducted with the long axis of the elements parallel to the applied field (easy axis). MR ratio was calculated using the expression, ΔR/R₀ = ((R – Rs)/Rs) x 100%, where R₀ is the resistance in zero field and Rs is resistance at saturation.

The GMR elements prepared using lift-off technique showed well-defined sidewall profiles without any remnants of bridging between the layer over the resist and layer over the substrate. This feature indicated that there were minimal interactions between the deposited structure and the resist. A concern for direct sputter deposition is significant shadowing effects due to background gas pressures during deposition. For example, for the background of Ar pressure of 10 mTorr, the height measured using stylus profilometer at the smallest
linewidth (0.5 µm) was found to be approximately 60% of unpatterned height. As shown in Figure 1.1, the optimal conditions were achieved at very low pressures (1-2 mTorr) where for the 0.5 µm, the height is approximately 95% of that of an unmasked area. A pressure of 2 mTorr was used during sputter depositions in order to enhance plasma stability during deposition. With optimal low background Ar pressures during sputtering, there still existed difference in effective deposition rate on linewidths, although this difference was minimal (≤5%). Due to this limitation, spin-valves and pseudo-spin valves were fabricated and deposited with thicker layers than the optimal metallic layer thickness found to maximize GMR ratio. Cross-sectional TEM (Figure 1.2) of a Co/Cu sandwich structure with Fe buffer layer showed a slight sloping, which can be quantified as a loss of 40% extending 800 Å from the edge.

Figure 1.3(a) shows the saturation magnetization versus line-width for two spin-valve multilayer structures, namely, Cu(50Å)/Co(50Å)/Cu(50Å)/NiFe(30Å)/Cu(20Å) and [Cu(50Å)/Co(50Å)/Cu(50Å)/NiFe(30Å)]x5/Cu(20Å). Solid lines depict the saturation values of unpatterned films. It is clear from this figure that the minimal shadowing effects at the edge of the elements had a very small effect on saturation magnetization (M_s) of the GMR elements and the values of M_s are comparable to those of the unpatterned film. It can also be seen from this data that the M_s of Cu(50Å)/Co(50Å)/Cu(50Å)/Ni_{0.8}Fe_{0.2}(30Å)/Cu(20Å) is larger than that of the repeated structure of [Cu(50Å)/Co(50Å)/Cu(50Å)/Ni_{0.8}Fe_{0.2}(30Å)]x5/Cu(20Å). This can be attributed to the fact that the roughness of subsequent layers in the repeated structure increases for sputtered films. Resistance (R) versus temperature (T) measurements carried out on these two structures with two different widths (0.5 mm and 20 mm) showed that
shadowing effects at the edge of the GMR elements had minimal effect on $R(T)$ and residual resistance values [Figure 1.3(b)]. Figure 1.3(c) shows the plot of MR ratios as a function of line-width for Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structures. According to this figure, MR ratios are independent of linewidths indicating that any processing effects are minimal down to 0.5 µm.

Figure 1.4(a) shows the hysteresis loops of a 0.8 µm wire fabricated from the Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structure, with applied field parallel and perpendicular to the axis at 20 K and 300 K. In this sandwich structure, the ferromagnetic layers are separated by a relatively thick spacer. At 50 Å spacer thickness, the coupling strength should be at minimum and the anti-parallel alignment may be induced by a difference in magnetization switching characteristics between the Co layer coupled to the Fe buffer layer and the top Co layer. At $T = 20$ K, the coercivity increased with decreased width from 110 Oe (2.2 µm wire) to 170 Oe (0.8 µm wire); the normalized remnant magnetization ranged from 0.75 to 0.93. The MR ratios of this sandwich structures with two widths are shown in Figure 1.4(b) as a function of applied field. In Figure 1.5(a) we show the normalized MR ratios of Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) samples as a function of applied field for various line-widths. Plotting MR vs. applied field for various linwidths allows comparisons of the MR value and its shape, which indicates how the magnetic reversal occurs. It is clear from the shapes of these plots that a complete saturation is much more difficult for narrower widths. Higher applied fields are needed to completely saturate the wire. According to GMR theory, the maximum MR value should indicate the maximum anti-parallel alignment where the greatest scattering would occur. Due to the presence of Fe buffer layer, the field corresponding to maximum MR ratio did not
correspond to the coercivity as measured by SQUID magnetometer and shown in Figure 1.5(b). The fact that the $H_C$ values are less than that of the field at maximum MR indicates that the layer with higher magnetization switches first. This behavior is consistent with anisotropy arguments.

As a comparison, we also examined the magnetic properties of pseudo-spin valve Cu(50Å)/Co(20Å)/Cu(60Å)/Co(50Å)/Cu(30Å) structures fabricated by e-beam evaporation. Figure 1.6(a) shows the results of magnetization measurement of 1.2 μm wide (closed square) and MR measurement of 1.1 μm wide (open circle) at 10 K of the Co/Cu-based pseudo spin-valves. The field of maximum MR and coercivity from SQUID magnetometer measurements of the same system as a function of line-width are shown in Figure 1.6(b). Unlike the Co/Cu sandwich described above, pseudo-spin valves achieve anti-parallel alignment by one layer’s thickness differing from the other, which in essence allows one layer to align with applied field either faster or slower than the other due to the difference in coercivities.

In summary, by employing direct deposition and lift-off, magnetic elements with width down to 0.5 μm were successfully fabricated. The results showed that sputter deposition through sub-micrometer opening and subsequent lift-off have minimal effect on the transport properties of the structures. Properties such as $M_S$ and physical height are approximately independent of their minimum feature sizes. Thus, for feature sizes down to 0.5 μm, sputter deposition and subsequent lift-off is a viable fabrication process for magnetic elements. Lift-off processing incurs minimal thermal stress on the underlying magnetic layers. This process benefits the resulting quality of the structures, since spin-valve
structures are very susceptible to inter-diffusion of spacer layer materials into the ferromagnetic layers.
Figure 1.1. (a) Normalized height vs. linewidths for various sputtering gas conditions.  
(b) AFM scans of lift-off test structures consisting of 0.6 µm lines with various line-spacing. These structures were sputter deposited at 2 mTorr.
Figure 1.2. Cross-section TEM of Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) structure. Left micrograph shows the cross-section far from edge (right micrograph). The edge structure shows slight sloping due to shadowing effects extending approximately 800Å from the edge. Note that due to similar Z values of Fe, Co, and Cu it is difficult to discern individual layers.
Figure 1.3.  (a) Saturation magnetization vs. line-width for two spin-valve multilayer structures, Cu(50Å)/Co(50Å)/Cu(50Å)/NiFe(30Å)/Cu(20Å) and [Cu(50Å)/Co(50Å)/Cu(50Å)/NiFe(30Å)]x5/Cu(20Å). Solid lines depict the saturation values of unpatterned films.

(b) Normalized resistance vs. temperature for 0.5 μm and 20 μm wire structures of Cu(50Å)/Co(20Å)/Cu(60Å)/Co(50Å)/Cu(30Å) and the difference between two wires.

(c) Plot of MR values vs. line-width for Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structures.
Figure 1.4.  (a) Hysteresis loops of Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structure of 0.8 µm wire at applied field parallel and perpendicular to axis at 20 K and 300 K.
(b) Typical MR vs. Applied Field for Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structure for two linewidths. \( \Delta \rho / \rho_0 = (R - R_s) / R_s \times 100\% \) as defined as MR where \( R_s \) is resistance at saturation.
Figure 1.5.  (a) Normalized MR vs. applied field of Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structures of various linewidths.  
(b) Plot of maximum MR and coercivity measurement from SQUID for Fe(50Å)/Co(50Å)/Cu(50Å)/Co(50Å)/Cu(20Å) sandwich structures of various linewidths.
Figure 1.6.  (a) Magnetization measurement of 1.2 µm wide (closed square) and MR measurement of 1.1 µm wide (open circle) at 10 K of Co/Cu pseudo spin-valve.  (b) Cu(50Å)/Co(20Å)/Cu(60Å)/Co(50Å)/Cu(30Å) field of maximum MR and coercivity from SQUID magnetometer measurements vs. line-width.
2. Comparative Study of Ni Nanowires Patterned by e-beam Lithography and Fabricated by Lift-off and Dry Etching Techniques

(Y.D. Park and D. Temple)

Using e-beam lithography techniques we have patterned Ni wire widths down to less than 100 nm. The patterning techniques were utilized either to fabricate nano-deposition masks for further direct deposition of Ni and subsequent lift-off or to deposit Nb wire structures used for Ar ion-mill etch masks on top of Ni thin films. The resulting Ni nanowire structures showed strong differences in transport as well as differing morphologies measured by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). In the case of fabricating nano-deposition masks, direct deposition of Ni was performed by magnetron sputtering, thermal evaporation, and e-beam evaporation. In the resulting nanowires, e-beam evaporated wires show the best residual resistance and magnetoresistance (MR) characteristics. AFM results showed the nanowires produced by evaporation to have granular structure. The nanowires fabricated by dry etching surpassed all nanowires fabricated by direct deposition and lift-off in both residual resistances and MR characteristics. In terms of longitudinal MR response, all nanowires displayed changes from saturation values, which indicated the formation of domain walls during magnetic reversal.

For all cases studied, wire structures were patterned by electron-beam lithography. These patterning process involve the use of a bi-layer (PMMA/PMMA-MAA) resist structure, which after exposure in a converted JEOL JSM-6400 Scanning Electron Microscope (SEM) and development and rinsing in MEK and MIBK solutions, produces an overhang structure which facilitates lift-off. The first attempts to produce wires involved direct sputter deposition through the bi-level resist via the collimating body. Sputter
deposition was conducted at 1 mTorr Ar pressure after reaching base pressures less than 1 x 10^{-8} Torr. The power used was 50 WDC resulting in an effective deposition rate of 0.2 Å/s onto a substrate held at room temperature. The sidewall profile from SEM micrographs was found to be smooth and near-vertical as seen from the test pattern circle which underwent the same preparation steps as the wire test structure. The sidewall profile indicated that the arriving sputtered species were adequately collimated and that there was minimal interaction between the deposited wire and resist due to the overhang bi-level resist structure. The above sputter deposition and lift-off process was compared with other deposition processes. Thermal evaporation and electron-beam evaporation of Ni showed markedly different physical characteristics. Thermal evaporation was conducted after reaching base pressures of 2 x 10^{-6} Torr and for electron beam evaporation with base pressures less than 1 x 10^{-8} Torr with typical rates of 0.5Å/s.

AFM micrographs for the evaporated Ni nanowires are shown in Figure 2.1. For both thermal and e-beam evaporation the wires have a granular structure and relatively rough sidewalls. One would expect transport in these structures to be less than ideal because of scattering at defects. An alternative to using a lift-off metallization process was to define a Nb etch mask by a similar lift-off process. The resulting Nb etch mask (typically 750 Å thick) was deposited by sputtering over a 500 Å Ni film also deposited by sputtering. After Nb lift-off metallization, the sample was ion-milled with a typical beam voltage of 500 V and with beam current and neutralizer current of 20 mA and 20-25 mA, respectively. The remaining Nb was removed by reactive ion etching (RIE) with CF₄/O₂ at an applied RF power of 30 W. This process produced almost perfect selectivity between Nb and Ni, as seen in the cross-section transmission electron micrograph (TEM) shown in Figure 2.2. The Ni
nanowire of approximately 75 nm in width sits on a mesa created by over etching of the Si substrate by ~200 Å. The remaining height of the Ni nanowire is approximately 500 Å, equivalent to the original thickness of the thin film. This thickness is a good indication that the RIE etch essentially removed all of the Nb without etching the Ni. The shape of the wire, especially the sidewall slope, either indicates that the Nb mask layer did not have a sharp profile or that re-deposition during etching occurred, of which the later is more likely since SEM images indicated sharp side profiles for directly sputtered structures.

Transport measurements using a Quantum Design PPMS using an AC bridge with injected currents less than 100 µA were conducted for various nanowires following definition of contacts and leads by photolithography and Au/Ge metallization produced by thermal evaporation and lift-off. The first nanowire considered was fabricated by sputter deposition, through the bi-level resist and subsequent lift-off. Such structures showed resistivities much higher (>3 times) than bulk samples, indicating a disordered structure with a high impurity and/or defect concentration. As expected from such high room temperature resistivities, the wire resistance was nearly temperature-independent from 300 K to 5 K. The highly disordered structure may stem from high differential pressures within the nano-masks themselves during sputtering. Evaporated Ni nanowires had better resistivities at room temperature. For thermally evaporated Ni nanowires, resistances vs. temperature scans were unsuccessful because the wire became ‘open’ at approximately 220 K. This behavior may suggest that the Si substrate was probed instead of the nanowire, but the MR response showed distinct differences in resistances when the injected current was parallel and perpendicular to the applied field (Figure 2.3). This temperature behavior suggests that the nanowire was not continuous as-deposited as was also evident from AFM images. The
possibility of damage to the nanowire during the temperature scans can be ruled out since the MR response was taken after the temperature sweep. The electron-beam evaporated nanowire showed a metallic behavior in that resistance decreased with a decrease in temperature (Figure 2.4(a)). The residual resistance of nanowire is 0.75 of the 300 K value (resistivity ratio of 1.337) while the residual resistance of thin films deposited under same conditions was 0.46 of the 300 K value (resistivity ratio of 2.17). Along with better resistance vs. temperature results than from thermally evaporated sample, the MR responses were better defined. The MR response at 10 K for nanowire axis 0°, 45°, and 90° to the applied field is plotted in Figures 2.4(b,c,d). Figures 2.4(b,c) show ±2000 Oe sweeps.

For the nanowires fabricated from sputter deposited thin films by etching using Nb as the etch mask, Figure 2.5(a) shows the resistance vs. temperature. As for the electron-beam evaporated nanowire, this behavior is metallic with residual resistance 0.30 of the resistance at 300 K (resistance ratio of 3.56) which compares to a sputtered Ni thin film with residual resistance of 0.22 of the resistance at 300 K (resistance ratio of 4.46). Comparing electron-beam nanowires and ion-milled nanowires of similar width (100 nm and 90 nm), the resistance ratio of etched nanowires is improved by almost a factor of three while the thin film (between electron-beam evaporation and sputter deposition) is improved only by a factor of two. MR response is also well defined at 10 K with an AMR value of approximately 1 % (figure 2.5(b)).

Ni wires with widths less than 100 nm were fabricated by various schemes. Although the dimensions were all comparable, physical and transport properties varied markedly. Nanowires were also fabricated by utilization of an etch mask, Nb, which was selectively removed by RIE, from sputter deposited Ni thin films. The variation in transport properties
was especially evident for wires grown by deposition through nanometer sized openings. Direct sputter deposition with lift-off processing showed great promise when examined with SEM and AFM because of the smooth sidewall profiles and continuous structures. However, transport measurements revealed the structures to be highly disordered, as evidenced by resistance vs. temperature data, in which resistance was found to be independent of temperature. Although considerable care was exercised to produce structurally sound nanowires (i.e. use of collimating body in efforts to minimize premature closing of the resist opening), direct sputter deposition and lift-off to fabricate these nanowires did not result in metallic samples which were suitable for transport characterizations.

The concern of elevated pressures within the nanometer-sized openings during sputtering was addressed by the use of deposition techniques at lower pressures. For the electron-beam evaporated nanowires, AMR characteristics were well defined in the longitudinal and transverse orientations, along with a metallic R vs. T behavior. From AFM studies, the evaporated nanowires were found to range from discontinuous (thermal evaporated) to a continuous collection of mound like structures (electron-beam evaporated). This result can be attributed to the fact that arriving evaporated species possess lower energies than sputtered species. Although for unpatterned film growth, elevated temperature substrate conditions are the norm, the use of PMMA resist layers limited the deposition temperature. Comparisons of the residual resistance indicated that lift-off metallization techniques, even for best cases, are less suitable than direct etch processes. Electron-beam deposited Ni nanowires patterned by lift-off showed a resistance at low temperature 0.75 times that of the room temperature value, as compared to the unpatterned thin film of 0.46.
By sharp contrast the resistance of Ni nanowires produced by Ar ion-milling at low temperatures was 0.30 of the room temperature value, as compared to the thin film ratio of 0.22. If all other conditions were equal, the increase in low temperature resistivity should be equal for both cases (i.e. the increase in resistivity should be attributed to an increase in surface scattering). The lift-off case increased by 49% while the ion-mill case increased by 35%. It is likely the difference can be attributed to the structure of the electron-beam lift-off nanowire. More specifically, the continuous string of islands produces a higher surface area than a continuous smooth structure such as in the sputtered ion-milled nanowire structure, thus leading to higher surface scattering. This conclusion was supported by the MR data. For the orientation where the axis of the nanowire is parallel to the applied field, the response should be a constant resistance for single domain wire structures. This constant response was not observed, but the evaporated nanowire showed a much more distinct change in resistance at higher applied fields when compared to the Ar ion-milled nanowire, indicating portions of the nanowire magnetization were not parallel with the nanowire axis (direction of injected current). The morphologies observed in the evaporated nanowire would suggest there are many sites where the domain walls can be pinned resulting in multi-domain structures. Another distinct difference in MR response occurred for the orientation where the nanowire axis is 45° to the applied field. For the evaporated nanowire, the response is of positive magnetoresistance character at high fields while the opposite was observed for the Ar ion-milled nanowires.

From comparisons of the residual resistivities and MR response, nanowires fabricated by selective Ar ion-milling of sputtered film resulted in the best structures. Although it can be argued that direct-deposition and lift-off avoids further patterning processes which can
alter underlying film qualities. However, for the deposition techniques we considered, the resulting structures from deposition through nanometer sized openings possessed physical and transport much inferior to that of unpatterned films.
Figure 2.1.  (a) 50 μm x 50 μm AFM micrograph of Ni nanowire fabricated by thermal evaporation and by lift-off.  
(b) Ni nanowire fabricated by electron-beam evaporation and by lift-off.
Figure 2.2. Cross-section TEM micrograph of Ni nanowire patterned by ion-milling using Nb as etch mask. The image shows that the remaining Ni thickness is approximately that of the original deposited thickness of 50 nm. Si mesa is created during ion-milling.
Figure 2.3. Resistance vs. Applied Field for Ni nanowire fabricated by thermal evaporation and lift-off. The data for the nanowire axis parallel (closed square) and perpendicular (open down triangle) to the applied field indicate AMR-like behavior at room temperature.
(a) Temperature (K) vs. ρ/ρ(T=300K) for e-beam evap. nanowire (~100nm) and e-beam evap. film.

(b) Wire Axis θ = 0 to H: ΔΩ (Ohms) vs. Applied Field (Oe) at T = 10K.
Figure 2.4. Ni nanowire fabricated by electron-beam evaporation and lift-off. (a) Normalized Resistance vs. Temperature of nanowire (closed circle) and thin film (open diamond). (b), (c), (d) MR response of nanowire at 10 K for $0^\circ$, $45^\circ$, and $90^\circ$ between nanowire axes and applied magnetic field.
Figure 2.5. Ni nanowire fabricated by ion-milling from sputter deposited Ni thin film using Nb as an etch mask. (a) Normalized Resistance vs. Temperature for nanowire and thin film. (b) MR response at 10 K to applied field for $0^\circ$, $45^\circ$, and $90^\circ$ orientations.
3. Fabrication of Exchange-biased Spin Valves with CoFeB Amorphous Layers

(T. Feng and J.R. Childress)

Amorphous magnetic thin films have been paid increasing attention for applications to giant magnetoresistance (GMR) spin-valve structures due to their low coercivity and high electrical resistivity. Amorphous magnetic materials can achieve lower coercivities than permalloy $\text{H}_{80}\text{Fe}_{20}$, which is commonly used as the soft ferromagnetic sensing layer in spin-valve multilayers. Coercivities of 0.7 Oe have been obtained in amorphous CoFeB films. Furthermore, the high resistivity of amorphous magnetic materials results in a larger resistance change and consequently, higher output signal for a given GMR ratio. Also, amorphous magnetic layers can potentially increase the GMR effect by minimizing current shunting through under layers and cap layers. Typically, the resistivity of amorphous CoFeB can be as high as $40 \, \mu\Omega\, \text{cm}^2$. Amorphous CoFeB spin-valve multilayers with a NiO exchange-biasing layer have been reported. Therefore, it is a worthwhile comparison to study amorphous CoFeB spin valves with FeMn-biasing layers.

All CoFeB spin-valve multilayer samples were prepared in a magnetron sputtering system with a base pressure of $1 \times 10^{-8}$ Torr and argon plasma pressure of 2 mTorr, and deposited on oxidized silicon substrates. The FeMn target was $\text{Fe}_{50}\text{Mn}_{50}$ at. % and no buffer or cap layers were used. As amorphous materials are metastable solids, a cooled substrate and high deposition rate are believed to be essential to their deposition. However, our x-ray diffraction measurements indicate that amorphous CoFeB was sustained for deposition rates as low as 0.34 Å/s using room-temperature substrates. An induced uniaxial anisotropy was
realized by applying a static magnetic field of about 600 Oe in the plane of the film during deposition and annealing.

Generally, the coercivity of crystalline magnetic films increases with decreasing thickness due to the increased influence of surface and interface defects on the magnetic reversal. In the case of multilayered amorphous CoFeB films, the interface “defects” may consist of crystalline or microcrystalline regions which are formed at the CoFeB or CoFeB/FeMn interfaces. For CoFeB/Cu/CoFeB/FeMn structures, soft magnetic properties are required for the free CoFeB layer only, while the pinned CoFeB for both layers is driven by the goal of increasing the overall resistivity. In our case, with \( t(Cu) = 100 \, \text{Å} \), the free-layer coercivity \( H_c \) at \( T = 1 \, \text{K} \) is found to be constant and smaller than the absolute accuracy of our magnetometer (a few Oe) down to layer thickness \( r \) of 50 Å. Below 50 Å, the coercive field increases sharply, to about 20 Oe for \( t = 30 \, \text{Å} \) and 40 Oe for \( t = 20 \, \text{Å} \). Consequently, we usually chose our minimum free-layer thickness to be 40 Å, so that its coercivity is less than 10 Oe. Additionally, we have studied the dependence of magnetic coupling on the Cu layer thickness. We find that when Cu is deposited at 1 Å/s, the observed free-layer coercivity begins to increase for \( t(Cu) \) below 50 Å and that the two CoFeB layers are strongly coupled for \( t(Cu) < 30 \, \text{Å} \). Thus, while the CoFeB films are amorphous, there appears to be sufficient interfacial roughness to cause significant magnetostatic coupling for \( t(Cu) < 50 \, \text{Å} \) and direct exchange coupling for \( t(Cu) < 30 \, \text{Å} \).

A typical hysteresis loop for a CoFeB(40 Å)/Cu(50 Å)/CoFeB(40 Å)/FeMn(100 Å) structure, deposited in a 600 Oe longitudinal field, is shown for \( T = 10 \, \text{K} \) in Figure 3.1 (open circles). The difference in the magnetic reversal of the two CoFeB layers is a combination of their difference in coercivity and the direct exchange coupling of the FeMn pinning layer. In
particular, the coercivity of the pinned layer is about 180 Oe, due to both its reduced thickness and proximity to the FeMn, while the exchange coupling measured by the loop shift is only about 30 Oe. Nevertheless, the 180 Oe wide plateau of the magnetization attests to the stable anti-parallel alignment of the two magnetic layers in that range. The coercivity of the free layer for this sample is about 10 Oe, due to its reduced thickness. It is interesting to note that the pinning effect of the FeMn layer was only obtained when grown on top of the structure. An identical sample with the FeMn layer on the bottom, also shown in Figure 3.1 (filled circles), reveals a simple hysteresis loop with a single reversal, and a coercivity intermediate between that of the two layers in the previous example.

The effect of the 600 Oe deposition field, which induces an in-plane uniaxial anisotropy of about 35 Oe in the CoFeB films, on the magnetoresistance (MR) characteristics, was examined for a CoFeB(40 Å)/Cu(40 Å)/CoFeB(20 Å)/FeMn(100 Å) structure, as shown in Figure 3.2. The structure deposited in a field (filled circles), as expected, displays abrupt reversals of both free and pinned CoFeB layers, with a well-defined antiparallel magnetization region over a field range of 150 Oe, with a GMR amplitude of about 0.5%. The structure deposited without a field, on the other hand, does not show any clear flat regions in its MR curve (open circles), which suggests that antiparallel alignment of the two CoFeB magnetizations is not achieved. Surprisingly, the maximum MR achieved in the latter case is twice that of the case where a field is applied, whereas one would expect that the maximum GMR effect would occur for a particular structure when perfect antiparallel alignment is achieved. This indicates that other characteristics, besides the magnetic reversal behavior, are different in the two samples. In fact, the overall resistivity at saturation of the structure deposited in a field increases by about 10% (10 mΩ
cm vs. 9 mΩ cm without a field), although this is not sufficient to completely account for the change in $\Delta R/R$.

A decrease of the Cu spacer thickness below 40 Å leads to increased coupling of the CoFeB layers, while a difference in thickness for the two CoFeB layers is required to maximize the coercivity contrast. For example, as shown in Figure 3.3 (open circles), the MR response of a CoFeB(30 Å)/Cu(30 Å)/CoFeB(30 Å)/FeMn(100 Å) sample deposited in a field, has the same magnitude (0.5%) as that of Figure 3.2, but only displays a broad maximum indicative of an overlapping switching of the magnetic layers. However, we have found that in that case a mild field annealing of the structure (2 h at 250°C) leads to a much higher GMR (1.2%), and to a decoupling of the CoFeB layers, as indicated by the resistance plateau observed at small negative fields (Figure 3.3, filled circles). This indicates a sharpening of the CoFeB/Cu interface upon annealing, leading to lower magnetostatic coupling, and an increase in the exchange pinning by FeMn, while the increase in GMR may indicate some recrystallization of the CoFeB, which is known to occur about 250°C.

Given the above results, the best combination of magnetic and MR properties has been achieved in a CoFeB(40 Å)/Cu(30 Å)/CoFeB(20 Å)/FeMn(100 Å) structure, as shown in Figure 3.4. Using different thicknesses for CoFeB, one can reduce the Cu thickness to 30 Å while retaining an independent reversal for the magnetic layers. The maximum observed MR ration at low temperatures is 1.2%, with a response field of less than 10 Oe. The above results confirm that CoFeB can be used as both a soft free layer, and as a pinned layer in conjunction with FeMn. While the MR amplitude is still very small, it is expected that additions to the CoFeB/Cu interface, such as thin Co or CoFe layers, can increase the
observed effect. Additionally, further engineering of the CoFeB/FeMn interface is required to obtain significant exchange coupling near room temperature.

In conclusion, the low-temperature magnetic and magnetotransport characteristics of CoFeB/Cu/CoFeB/FeMn spin valves have been investigated. Decoupling of the CoFeB magnetizations can be achieved for Cu thicknesses as low as 30 Å with proper magnetic-field biasing during depositions and/or postdeposition annealing treatment. The resulting GMR effect is small (<1.2%), but appears to be very sensitive to the details of the deposition procedures.
Figure 3.1  Hysteresis loop for CoFeB (40Å)/CoFeB(20Å)/FeMn(100Å) (open circles) and FeMn(100Å)/CoFeB(20Å)/Cu(50Å)/CoFeB(50Å)/Cu(50Å) (filled circles), measured at $T = 10$ K.

Figure 3.2  Magnetoresistance loop for CoFeB(40 Å)/Cu(40 Å)/CoFeB(20 Å)/FeMn(100 Å) deposited with a 600 Oe planar magnetic field (filled circles) and without a magnetic field (open circles), measured at $T = 10$K.
Figure 3.3. Magnetoresistance loop for CoFeB(30 Å)/Cu(30 Å)/CoFeB(30 Å)/FeMn(100 Å) with a postdeposition annealing of 2 h at 250°C (filled circles) and without a postannealing (open Circles), measured at $T = 10K$.

Figure 3.4. Magnetoresistance loop for CoFeB(30 Å)/Cu(30 Å)/CoFeB(30 Å)/FeMn(100 Å) measured in a maximum magnetic field of 5000 Oe (closed circles) at $T = 10K$. 
4. Cl$_2$-based Dry Etching of Doped Manganate Perovskites:

PrBaCaMnO$_3$ and LaSrMnO$_3$


It has long been known that bulk ceramic and single-crystal specimens of hole-doped manganites of the basic perovskite structure La$_{1-x}$M$_x$MnO$_3$ (where M is typically Ba, Sr, Ca or Pb) display a large magnetoresistance (MR). The subsequent discovery of a large room-temperature MR in thin films of doped manganate perovskite opened up the possibility of applications in read heads for hard disk drives, sensors and magnetic random access memories (MRAM). This was followed by the reports of a very large negative MR at 77K in thin film La$_{0.67}$Ca$_{0.33}$MnO$_3$, termed colossal magnetoresistance (CMR). Currently most efforts are focussed on obtaining high MR ratios at lower magnetic fields than in the original reports (6T) and at higher temperatures. Chemical substitution on the trivalent site is observed to improve MR behavior, since interatomic distance influences the magnetic-exchange interactions between the cations. Therefore, Nd- and Pr-based manganites are expected to show improved MR behavior relative to La-based compounds. In addition large MR values have been achieved in LaMMnO$_3$/SrTiO$_3$/LaMMnO$_3$ trilayers (M = Ca or Sr) at low fields.

To fabricate spin-valve read heads or MRAM elements it is necessary to develop pattern transfer processes for the manganites. In conventional NiFe-based giant magnetoresistance materials, the patterning is generally performed by ion beam milling because of the relatively low volatility of metal halide etch products. We have previously reported that Cl$_2$/Ar discharges operated under high density plasma conditions can provide practical etch rates for NiFe and related materials. Very little work has been performed in the
CMR materials. In LaCaMnO$_3$ we found that iodine and bromine plasma chemistries proved some degree of chemical enhancement in the etch mechanism.

La$_{0.64}$Sr$_{0.27}$MnO$_3$ thin films were prepared on LaO (001), MgO (001) single crystal substrates by liquid delivery metallo-organic chemical vapor deposition (LD-MOCVD) as follows:

An NZ-Applied Technologies liquid delivery vaporization system was used to deliver the 2, 2, 6, -tetramethyl-3, 5-heptanedionato (TMHD) organometallic precursors; La(TMHD)$_3$, Mn(TMHD)$_3$, and Sr(TMHD)$_2$ which were dissolved in 25 ml of freshly distilled solvent (diglyme) and vaporized (T = 230ºC) at a rate of 1.66 µl·min$^{-1}$. The gaseous mixture was then introduced into an EMCORE reactor. N$_2$ (100 sccm) served as a carrier gas. O$_2$ (600 sccm) and N$_2$O (500 sccm), introduced directly into the reaction chamber, served as oxidants. During the deposition the substrates were held at a temperature of 700ºC and the reactor pressure was maintained at 5 Torr. After deposition, the films were slowly cooled under reaction conditions until the susceptor temperature was below 100ºC when the substrates were removed. No post annealing was performed on the films. The deposition rate was approximately, 15 Å·min$^{-1}$. The deposition process for all films was between 60 to 70 minutes, resulting in films of approx. 1000 Å.

Thin films of Pr$_{0.65}$Ba$_{0.05}$Ca$_{0.3}$MnO$_3$ were deposited on Si(100) or LaMnO$_3$(100) structures in a pulsed laser ablation system (248 nm KrF laser, 10 kHz, 2.5 J·cm$^{-2}$ energy density), at a substrate temperature of 700ºC and an O$_2$ partial pressure of 250 mTorr.

Etching was performed in a Plasma Therm 790 system with the samples thermally bonded to a He backside-cooled, rf-powered (13.56 MHz) chuck. The plasma was generated in a cylindrical geometry, three-turn coil source operating at 2 MHz and powers up to 1000
The Cl₂ and Ar were injected into the ICP source through electronic mass flow controllers at a total gas load of 15 standard cubic centimeters per minute (sccm). The process pressure was held constant at 5 mTorr. Etch rates were obtained by stylus profilometry after removal of the mask material (either Apiezon wax or plasma enhanced, chemically vapor deposited SiNx), while surface morphology and anisotropy were examined by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Figure 4.1 shows the effect of Cl₂ percentage (by flow) on the etch rate of the CMR materials in Cl₂/Ar discharges at fixed source power (750 W) and chuck power (250 W). The dc self-bias on the chuck increases as the Cl₂ percentage decreases due to the electronegative nature of chlorine reducing the positive ion density in the discharge. The etch rate trends are opposite for the two materials: for LaSrMnO₃ the rate goes through a maximum as the Cl₂ percentage increases, which suggests there is a degree of chemical enhancement in the etch mechanism but also that an optimal ion/neutral ratio is required. By contrast, for PrBaCaMnO₃ the rates with Cl₂/Ar are slower than for pure Ar. This indicates that the adsorption of Cl neutrals on the surface produces fairly involatile species and blocks the Ar⁺ ion bombardment. The fact that in both cases the etching requires a strong physical component is obvious from the etch yields (defined as the number of substrate atoms removed per incident ion at the ion energies employed here, which is 275 eV, comprised of the dc self-bias and plasma potential), which are low (<0.3) under all conditions.

The effect of rf chuck (which controls ion energy) on material etch rates is shown in Figure 4.2 for fixed discharge composition (10 Cl₂/5 Ar) and source power (750 W). In the case of LaSrMnO₃ the etch rates increase quickly as the dc self-bias increases, suggesting that the etching is limited by bond-breaking and product desorption. In the case of PrBaCaMnO₃,
the etch rates saturate above ~250 W. This is a fairly common observation in high density etching, and is usually ascribed to desorption of the absorbed neutral chlorine atoms before they can react with the thin film material.

The ICP source power controls the ion flux incident at the sample position. Figure 4.3 shows the influence of this parameter on materials etch rates in 10 Cl_2/5 Ar discharges at fixed rf chuck power (250 W). As the source power increases it creates more positive ions in the discharge and decreases the dc chuck self-bias. Since these leads to a decrease in incident ion energy, the resultant etch rates decrease for PrBaCaMnO_3 as source power increases. In the case of LaSrMnO_3, there is a trade-off between higher rates with increasing ion flux, and lower rates with decreasing ion energy. This leads to a maximum in etch rate at ~750 W source power. Therefore it is necessary to employ both high ion energy and ion flux for effective etching of the CMR materials.

The etched surface morphologies were a strong function of the plasma conditions. Figure 4.4 shows AFM scans before and after etching of the PrBaCaMnO_3. At the high Cl_2 percentage (lower left) the surface becomes substantially rougher than the as-deposited sample. However, under optimized conditions (in this case lower Cl_2 percentage in the discharge) the root-mean-square (RMS) roughness can actually be smoother than the control sample. This is due to the angular dependence of physically dominated etch processes, which leads to removal of sharp features faster than flat regions on the PrBaCaMnO_3.

Similar results were obtained for the LaSrMnO_3, as shown in the AFM scans of Figure 4.5. Note that the RMS values for the control samples for both materials are relatively high, but this is because they were grown especially thick for the etching studies. The RMS values are plotted in Figure 4.6 for both materials: these is clearly an optimum condition at the
lower Cl₂-to-Ar ratio. This reflects the need to provide some balance of atomic chlorine adsorption and the subsequent ion-assisted desorption of the chlorinated etch products. If the etching is too physically dominated then preferential sputtering of the lighter elements can occur, whereas if the Cl₂ percentage is too high, a selvedge or reaction layer will build up on the sample surface. Some examples of etched features are shown in the SEM micrographs of Figure 4.7. The pattern transfer into LaSrMnO₃ is anisotropic (top), and since the etch rates are reasonable, the etch time is sufficiently short that erosion of the SiNx mask is not a significant problem. In the case of PrBaCaMnO₃ (center and bottom), the slower etch rates lead to longer process times and problems with mask erosion that produces rough sidewalls or trenching, depending on the ion energy. However these micrographs clearly show the ability of the ICP Cl₂/Ar process to produce sub half-micron features in both CMR materials.

High density plasma etching of PrBaCaMnO₃ and LaSrMnO₃ in Cl₂/Ar discharges has been investigated. There is some degree of chemical enhancement relative to pure Ar sputtering present for LaSrMnO₃. The etch rates of both materials are strong functions of ion flux, ion energy and plasma composition (i.e. ion-to-neutral ratio). Some degree of surface smoothing can be achieved under optimized conditions, and sub-micron features are easily produced using SiNx or a mask. This process appears promising for patterning of CMR elements.
Figure 4.1. Etch rates (top) and etch yields (bottom) for PrBaCaMnO$_3$ and LaSrMnO$_3$ as a function of Cl$_2$ percentages in ICP Cl$_2$/Ar discharges (750 W source power, 250 W rf chuck power, 5 mTorr).
**Figure 4.2** Etch rates (top) and etch yields (bottom) for PrBaCaMnO$_3$ and LaSrMnO$_3$ as a function of rf chuck power in ICP 10 Cl$_2$/5 Ar discharges (750 W source power, 5 mTorr).
Figure 4.3. Etch rates (top) and etch yields (bottom) for PrBaCaMnO$_3$ and LaSrMnO$_3$ as a function of source power in ICP 10 Cl$_2$/Ar discharges (250 W rf chuck power, 5 mTorr).
Figure 4.4. AFM scans of PrBaCaMnO$_3$ before and after etching in ICP Cl$_2$/Ar discharges (750 W source power, 250 W rf chuck power, 5 mTorr).
Figure 4.5. AFM scans of LaSrMnO$_3$ before and after etching in ICP Cl$_2$/Ar discharges (750 W source power, 250 W rf chuck power, 5 mTorr).
Figure 4.6. RMS surface roughness as a function of Cl$_2$/Ar relative flow rates after etching in ICP discharges (750 W source power, 250 W rf chuck power, 5 mTorr).
Figure 4.7. SEM micrographs of features etched into LaSrMnO$_3$ (top) or PrBaCaMnO$_3$ (center and bottom) using 5 Cl$_2$/10 Ar, 750 W source power, 5 mTorr discharges at either 250 W (top and center) or 150 W (bottom). The SiN$_x$ masks are still in place. The feature width is 0.35 µm in each case.
5. Long Term Stability Of Dry Etched Magnetoresistive Random Access Memory (MRAM) Elements


Most of the experiments were performed with the MRAM structure shown in Figure 5.1. The SiO$_2$ and SiN$_x$ layers were grown on Si substrates by chemical vapor deposition, followed by Ar$^+$ ion-assisted sputtering of the magnetic multilayers. The structure was completed with anti-oxidation and contact layers (Ta, TaN, CrSi) and a 3000Å thick SiO$_2$ mask patterned by SF$_6$/Ar RIE was employed as the etch mask for ICP etching. In some cases we also deposited single, 500Å thick, layers of Ni, Ni$_{0.8}$Fe$_{0.2}$ or Ni$_{0.8}$Fe$_{0.13}$Co$_{0.07}$ on Ta buffers on Si substrates to examine their magnetic properties after dry etching.

All etching was performed in a Plasma Therm 790 ICP system, in which the discharge is created in a 2MHz, 3-turn coil source operating at 500W. The samples were thermally bonded to a He backside-cooled, rf powered (13.56MHz, 250W) chuck. A mixture of 10Cl$_2$/5Ar at a total gas load of 15 standard cubic centimeters per minute (sccm) was injected into the ICP source through electronic mass flow controllers. The etch time for the MRAM stacks was ~1.5mins. The single layer structures were exposed to pure Ar discharges at the same power conditions used for etching the multilayers in order to simulate the ion-induced damage.

The magnetic properties before and after plasma processing were determined using SQUID magnetometry (Quantum Design MPMS-5S) at 4.2K. As a “control” sample, we took a small (1×2mm$^2$) piece of the unpatterned MRAM structure. Normally one would take a sample patterned with a process that was known to create no damage on the magnetic multilayers and hence would not degrade the magnetic performance. However, as discussed
below, ion milling has been found to affect the coercivity of small (micron-size) MRAM elements, and wet chemical etching is insufficiently controlled at these dimensions. Therefore we measured the patterned area on the dry etching samples by SEM, and normalized the data to the number of spins in the control (unpatterned) and etched (patterned) samples. Samples were measured approximately every month for 6 months after initial plasma exposure. Scanning Electron Microscopy (SEM) and Auger Electron Spectroscopy (AES) were also used to examine the long-term stability of the corrosion-prevention treatments.

It has previously been found that the coercivity of MRAM elements can be severely increased (by up to a factor of eight) when high energy (1000eV) Ar\(^+\) ion milling is used for pattern transfer, relative to lower energy (300eV) milling. Under our ICP conditions, the average incident ion energy is \(~200eV\). To examine the effect of this ion bombardment on magnetic properties, the single layer Ni, NiFe and NiFeCo samples were exposed to the ICP Ar discharge. The sputter rate of all three films was \(~8Å\cdot sec\(^{-1}\) under our conditions. Figure 5.2 shows the saturation magnetization to be independent of remaining Ni, NiFe or NiFeCo thickness, which indicates the plasma exposure is not creating significant “magnetically-dead” regions ahead of the etch-front. We note that damage in this direction vertical to the incoming ion is expected to be much worse than damage to the sidewalls of etched features, due to the low process pressure (2mTorr) and consequent minimization of ion scattering that might cause divergence from the expected vertical angle of incidence. Moreover, in a real etch process there would be less damage due to the presence of some chemical enhancement and consequent higher etch rate, reducing the possibility of damage accumulation.
Turning to the Cl₂/Ar etched MRAM stacks, we have previously found that severe corrosion occurs on the edges of the elements if no specific steps are taken to avoid this, as shown in the SEM micrographs of Figure 5.3. In this case the samples were patterned with the Cl₂/Ar process, and simply stored in air. The SEM micrographs were taken approximately two weeks later, and show the classic signs of metal corrosion.

To counteract this problem, four different post-etch treatments were examined. The first was simply rinsing the samples in de-ionized water immediately upon opening the chamber (which is contained within a N₂ dry box). The samples were then thoroughly dried with filtered N₂. In the other three methods, various in-situ plasma cleaning procedures were examined. After the Cl₂/Ar etching was complete, the chamber was evacuated for 15mins, and then a 30mTorr discharge of either H₂, O₂ or SF₆ (500W source power, 5W chuck power) was used to clean the residual chlorine for 10mins prior to removed or the samples from the reactor. In these cases, no H₂O rinsing was performed. It should be pointed out that all of these cleaning procedures have been employed previously for removing etch residues after Cl₂-based plasma etching of Al interconnects in Si microelectronics.

Figure 5.4 shows some typical SQUID data for MRAM samples before and after Cl₂/Ar etching and subsequent cleaning. We assume the hysteresis in the control sample is related to some inhomogeneity in materials properties, relative to the smaller volume sampled in the patterned structures. The data for the SF₆ cleaned sample was similar to that for H₂ cleaning. The data was normalized to the remaining volume of magnetic material after patterning, and the results are shown in Figure 5.5. Within experimental error, there is no change in the magnetization per unit volume for any of the samples except that treated in O₂. A possible interpretation of this is that the feature sidewalls become more oxidized than with
the other treatments, leading to a degradation of the magnetic properties. The results of Figure 5.5 are clear evidence that a magnetic multilayer structure can be patterned by dry etching under optimized conditions (i.e. post-etch H₂O rinse, or H₂ or SF₆ in-situ plasma cleaning) without any fall-off in the magnetic performance of the structure.

We believe the fall-off in magnetization of the O₂ plasma exposed sample is not a result of residual chlorine and subsequent corrosion for two reasons. Firstly, Figure 5.6 shows AES surface scans of single layer NiFe samples exposed to the Cl₂/Ar discharge, and then cleaned for 5mins using the different treatments material above. There are significant amount of residual chlorine on the H₂ and SF₆ treated samples, but with either water rinsing or O₂ plasma exposure, the Cl₂ signal is at the detection limit. These results show that O₂ is more effective per unit time in removing chlorine residues than either H₂ or SF₆. The second reason is the excellent long-term stability of all of the cleaned samples, showing that there is no corrosion. After 10 min cleans (as used in the final, optimized process), we detected only the lattice elements on each sample and no Cl-related residues were found.

Figure 5.7 shows the magnetization of each of the samples over an extended period. In each case the samples were simply stored in air between the measurements and no special precautions were taken to prevent corrosion. Each of the cleaning procedures produces samples with extremely stable magnetic characteristics. This is also reflected in their appearance. The control sample was similarly stable with time. If we did not use any of the cleaning procedures after dry etching, corrosion quickly (<7 days) destroyed the samples, and we were unable to measure the magnetic properties. In some cases, the metal stack corroded within 24 hours (under more Cl₂-rich plasma conditions), while for the standard 10Cl₂/5Ar conditions, the corrosion took 5-7 days to destroy the samples. Figure 5.8 shows SEM
micrographs of patterned MRAM elements 6 months after Cl$_2$/Ar etching and post-etch cleaning. There is no indication of corrosion on any of the samples.

The main conclusions of this study on dry etched MRAM elements are as follows:

1. ICP etching does not have any measurable effect on the magnetic quality of thin film Ni, NiFe or NiFeCo, with any “dead layers” being <50Å in thickness. Similarly, ICP-etched MRAM multilayer stacks show no change in magnetic properties from thin control values, provided chlorine residues are removed.

2. Post-etch rinsing in H$_2$O or in-situ plasma cleaning with H$_2$, O$_2$ or SF$_6$ discharges are all effective treatments for removing chlorine etch residues. Of these, only O$_2$ plasma exposure appears to degrade the magnetic properties of MRAM stacks. Once the residues are removed, there is no change in magnetic or visual properties over a period of ~6months (extent of our study).

3. The combination of Cl$_2$/Ar ICP etching and post-etch cleaning provides an effective pattern transfer method for magnetic multilayers.
**Figure 5.1.** Layer structure of MRAM element. The top SiO$_2$ layer is the mask for ICP etching of the underlying layers. Etching terminates on the 300Å thick SiN$_X$ layer.
Figure 5.2. Saturation magnetization versus thickness removed by etching in 500Å thick films of Ni, NiFe and NiFeCo.
Figure 5.3. SEM micrographs of Cl$_2$/Ar etched MRAM elements taken about two weeks after etching. For these samples, no post-etch cleaning of chlorine residues was performed.
Figure 5.4. Hysteresis loops for MRAM structure before and after ICP Cl₂/Ar etching, and subsequent cleaning for 10mins either by H₂O rinsing or exposure to H₂ or O₂ plasmas prior to removal from the etch reactor.
Figure 5.5. Magnetization per unit volume for MRAM structure before and after ICP Cl2/Ar etching, and subsequent cleaning for 10mins either by H2O rinsing or exposure to H2, SF6 or O2 plasmas prior to removal from the etch reactor.
Figure 5.6. AES surface scans from NiFe samples exposed to ICP Cl₂/Ar plasmas and subsequently cleaned for 5mins either by H₂O rinsing or exposure to H₂, SF₆ or O₂ plasmas prior to removal from the etch reactor.
**Figure 5.7.** Magnetization of MRAM structures, either unetched or etched in ICP Cl₂/Ar plasmas and subsequently cleaned in H₂O or H₂, SF₆ or O₂ plasmas, as a function of storage time in room ambient.
Figure 5.8. SEM micrographs of MRAM elements after etching in ICP Cl₂/Ar plasmas and subsequent cleaning in H₂, SF₆ or O₂ discharges or by H₂O rinsing. The micrographs were taken 6 months after these processes, with the samples having been stored in room ambient.
6. **Inductively Coupled Plasma and Electron Cyclotron Resonance Plasma Etching with CO/NH$_3$ Chemistry**

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In an attempt to increase the volatility of the magnetic materials etch products, Kinoshita et. al. reported use of elevated substrate temperatures during RIE. While the etch rate at ~380°C was a factor of three larger than pure Ar$^+$ ion milling, this temperature is unacceptably high for many magnetic structures, particularly multilayers of the type used in Giant Magnetoresistance (GMR) devices. An alternative method of providing the energy needed to desorb the etch products is use of high ion density plasmas. The ion flux in these tools is 2-3 orders of magnitude higher than in RIE systems, and thus it is possible to operate in a regime where there is a balance of etch product formation and the immediate ion-assisted desorption of these products. In this situation there is no build-up of a reaction or selvedge layer on the sample surface, which in RIE actually produces net deposition rather than etching.

While Cl$_2$-based plasma chemistries operated under high density conditions provide practical etch rates for NiFe and Al$_2$O$_3$-TiC, there is always a concern with corrosion caused by plasma residues that remain on feature sidewalls upon removal from the reactor. Nakatani reported use of a non-corrosive CO/NH$_3$ plasma chemistry for NiFe, in which the etch products are expected to be carbonyls (e.g. Fe(CO)$_5$). The resultant etch rates were $\leq 300\AA\ \text{min}^{-1}$ for Ni$_{0.8}$Fe$_{0.2}$, a factor of about three higher than purely physical Ar$^+$ sputtering under the same conditions. The reactor employed was non-commercial, and might be classified as a magnetron-type, medium ion density system.
In this section we report on a parametric investigation of CO/NH$_3$ etching of NiFe, NiFeCo and related thin film materials using either an Inductively Coupled Plasma (ICP) reactor which is the preferred embodiment of the high density source because of its excellent scalability and uniformity, ease of tuning and absence of bulky, expensive electromagnets or an Electron cyclotron Resonance (ECR) reactor. We find maximum etch rates for NiFe and NiFeCo in the range 350-400 Å·min$^{-1}$ in ICP system and 500 Å·min$^{-1}$ in ECR system, with the rates being a strong function of CO:NH$_3$ ratio, source and rf chuck power and pressure. We also compared use of CO$_2$ to replace CO, though this does not appear to offer any advantage in etch rates. Finally, the selectivity for etching the magnetic materials over common mask materials (photoresist, SiO$_2$) was measured over broad range of conditions.

One of the key results in Nakatani’s work was that NH$_3$ was needed in the plasma chemistry to prevent dissociation of the CO. If the latter occurs, then it would block formation of the metal carbonyl etch products. To examine the species created in ICP sources, optical emission spectroscopy (OES) was employed. Figure 6.1 shows that there is a significant difference in the spectra obtained from CO/NH$_3$ and CO$_2$/NH$_3$ discharges. In the latter case only two dominant lines (486 and 660nm) due to atomic hydrogen are observed. By sharp contrast, the CO/NH$_3$ spectra is dominated by the NH$_3$ component, which in turn comprises the N° transitions (300-400nm) and the N$_2^+$ and N$^+$ components (550-700nm) together with the atomic H° lines. There is no indication of the dissociation of the CO or CO$_2$, and for pure discharges of these feed gases we observed only broad molecular continuum.

Figure 6.2 shows etch rates of NiFe and NiFeCo in 2CO/13NH$_3$ and 2CO$_2$/13NH$_3$ discharges (250W rf chuck power, 2mTorr process pressure) as a function of source power.
Note that at zero watts source power, which corresponds to reactive ion etching, the etch rates are negligible. The rates increase with source power as both the ion flux and plasma dissociation efficiency increases. At the highest powers the rates fall-off, probably due to a combination of reduced ion energy as the plasma conductivity increases and to sputter-desorption of the reactants before they can react with the surface of the magnetic materials. The selectivity for NiFe and NiFeCo over Al₂O₃ under these conditions is ≤40. Note that the CO/NH₃ chemistry produces faster rates than CO₂/NH₃ over a broad range of conditions, presumably because the CO species is the active etchant.

To determine whether there is a significant chemical component to the etching with CO/NH₃, we compared etch rates with purely physical chemistries (Ar and N₂). For these and all subsequent experiments the cathode area was reduced (from 8 to 4 inch diameter) to increase the power density in the plasma and enhance the physical component of the etching. Figure 6.3 shows etch rates of NiFe and NiFeCo in the three plasma chemistries as a function of either source power (top) or rf chuck power (bottom). There is a very clear conclusion from this data—the rates with CO/NH₃ are lower than those with Ar, showing that the chemical enhancement with the former is not large. However a better comparison is between N₂ and CO/NH₃ since the heaviest ion in both mixtures has mass 28 (N₂⁺, CO⁺). In this comparison, it is seen that there is indeed some chemical enhancement with the CO/NH₃. Note that at high rf powers or source powers we actually observe net deposition on NiFe exposed to N₂ plasmas, possibly due to formation of surface nitrides. Surface analysis by Auger Electron Spectroscopy shows only the presence of the Ni, Fe plus C, O and N.

Each of the main plasma parameters was systematically varied to determine the effect on Ni₉₈Fe₀₂ etch rate and the selectivity relative to SiO₂, which as we will see later is the
The most appropriate mask material. Figure 6-4 shows the effect of CO percentage in the discharge (top) and of process pressure (bottom). The NiFe etch rate initially increases as CO is added to the discharge, but then decreases at CO-rich conditions. This is consistent with the result from Nakatani that NH$_3$ is needed to assist in the formation of the metal carbynlys. The etch selectivity relative to SiO$_2$ depends on the how the SiO$_2$ was produced-thermal oxide has significantly lower etch rate than deposited oxide and consequently produces higher selectivity for NiFe over SiO$_2$. Similar trends are observed with process pressure-initially the NiFe etch rate increases as more reactants are available, but above ~2mTorr the rates decrease due to increased recombination in the discharge.

Figure 6.5 shows the effect of source power (top) and rf chuck power (bottom) at fixed discharge composition. The same trend as discussed earlier for lower CO contents (Figure 6.2, where 2CO/13NH$_3$ discharges were employed) were observed, with the etch rates decreasing at high source powers. The fact that the etch mechanism is still physically dominated is clear from the lower part of the Figure, where the NiFe etch rate increases monotonically with rf power. Note that selectivities in the range 5-8 are obtained relative to thermal SiO$_2$.

The effect of substrate temperature is shown in Figure 6.6. The NiFe etch rate continues to increase with temperature as the vapor pressure of the metal carbynlys increases and they are more effectively removed from the surface. A rate of 400Å·min$^{-1}$ was obtained at 175°C, where the selectivity to thermal oxide falls off rapidly to the value for deposited oxide. Note that selectivities are ≤10 in all cases for both oxides.

The new generations of magnetic memories and storage devices are based on GMR multilayers comprising materials such as NiFe, NiFeCo, TaN, Cu and CrSi. A key question is
whether the CO/NH\textsubscript{3} plasma chemistry can also etch the latter three materials. Figure 6.7 shows the effect of source power (top) and rf chuck power (bottom) on material etch rates. While Cu etches faster than NiFe, the rates for both TaN and CrSi are basically just due to physical sputtering and there is no chemical component to their removal mechanism. For the type of GMR structures used for magnetic recording, the individual layers are only 50-250Å thick, and therefore etch rates of 100Å min\textsuperscript{-1} are probably acceptable.

As mentioned earlier photoresist does not hold up well in the CO/NH\textsubscript{3} discharges. Some typical etch rate data is shown in the top part of Figure 6.8 for variation of source power. The photoresist typically etches at a rate 10-20 times faster than NiFe and NiFeCo. By contrast, the etch rates for SiO\textsubscript{2} are much lower (some typical data are shown in the lower part Figure 6.8 for variation of rf chuck power), indicating that this is the most appropriate mask material.

For a typical GMR multilayer (CrSi/NiFe/Cu/NiFeCo/TaN) with total thickness ~2,000Å, the CO/NH\textsubscript{3} chemistry can provide clean, effective pattern transfer using SiO\textsubscript{2} masks, as shown in the SEM micrograph of Figure 6.9. Even though the etching is still physically-dominated, the etch time is short enough that mask erosion is not significant. There was no long-term (3 months) corrosion observed on these samples, as expected due to the non-corrosive nature of the plasma chemistry.

By contrast, if very deep (>1µm) etch depths are required, then erosion of the SiO\textsubscript{2} mask becomes noticeable. Figure 6.10 shows features etched ~1µm deep into NiFe using CO/NH\textsubscript{3}. The dimpling on the mask area was not a result of the plasma etch process, but was visible on the pre-etched samples. Facetting of the SiO\textsubscript{2} mask leads to sloped, rough
sidewalls on the etched features, and will present a severe problem for making small-
dimension structures.

Figure 6.11 compares NiFe and NiFeCo etch rates in CO/NH$_3$ (top) and CO$_2$/NH$_3$
(bottom) ECR discharges (750W source power, 250W rf chuck power, 2mTorr pressure) as a
function of discharge composition. There are significant differences in behavior between the
two chemistries, but they display the same basic trend of increase in etch rate as CO or CO$_2$
is initially added to the discharge, followed by a fall-off to net deposition at low NH$_3$
compositions. The initial etch rate increase as CO or CO$_2$ is added is indicative of some
degree of chemical enhancement due to these gases, which was confirmed by a comparison
with pure N$_2$ discharges. The heaviest ion in N$_2$ or CO/NH$_3$ discharges should have mass 28
(N$_2^+$ or CO$^+$). (It is possible in some cases to have ion-molecule reactions with large cross-
sections can give molecular ions such as I$_2^+$ in iodine-containing discharges. However the
gas mixtures in this study are unlikely to give any molecular ions heavier than additional
hydrogen attachment to CO$^+$). A sputter rate for NiFe of $\sim$350Å·min$^{-1}$ was obtained for pure
N$_2$ discharges under these conditions, which is less than the maximum rate obtained using
CO/NH$_3$. By analogy with the work of Nakatani, the fact that the process reverts to net
deposition at high CO or CO$_2$ concentrations may be due to the creation of a carbided
surface. Some evidence for this comes from the AES surface scans of Figure 6.12. After
exposure to a CO/NH$_3$ plasma at conditions where there is net deposition, there is additional
C and N detected on the surface due to polymer or carbide formation that prevents etching.

We could not detect any measurable differences in the optical emission spectra from
pure CO and CO$_2$ discharges (Figure 6.13). There appears to be a line at $\sim$780nm due to
atomic oxygen. Unfortunately many of the CO and CO$_2$ transitions are below 300nm, where
our spectra are cut-off by the quartz viewport on our system. As NH$_3$ is added to the discharge (Figure 6.13, bottom), there is the appearance of atomic hydrogen transitions at 480 and 660nm and the nitrogen-related bands between 300-400nm. At NH$_3$-rich conditions where etching of the magnetic materials occur, the spectra is completely dominated by N$_2$ and H transitions. Therefore optical emission spectroscopy does not appear that useful for tracking the active species in the plasma.

Figure 6.14 shows the effect of microwave source power on the etch rates of NiFe and NiFeCo for two different plasma compositions at fixed rf chuck power (250W) and process pressure (2mTorr). At low CO to NH$_3$ ratios (2/13) the etch rates increase with source power (which controls ion flux and dissociation of the discharge) and then decrease beyond ~750W. The dc self-bias decreases as plasma conductivity increases, but the fall-off in etch rate at high source power is most likely due to the onset of surface carbidation. This would be consistent with the data in the lower part of the Figure, where a transition to net deposition occurs at much lower source powers in CO-rich discharges.

The role of ion energy on the NiFe and NiFeCo etch rates is shown in Figure 6.15. The sum of dc self-bias and plasma potential (~25eV in this tool) is the average energy for ions striking the sample. As rf chuck power is increased the dc self-bias increases, but the etch rates fall-off above particular ion energies (~450eV for the 2CO/13NH$_3$ condition and ~400eV for the 10CO/5NH$_3$ condition). This is often observed in high density plasma etching, and is usually ascribed to desorption of the reactive neutrals by ion-assistance before they can react with the sample surface. In the CO/NH$_3$ chemistry the high ion energy conditions may also lead to dissociation of the adsorbed CO species, because the process reverts to net deposition under CO-rich conditions.
Examples of the effect of process pressure are shown in Figure 6.16 for two different plasma compositions at fixed source power (750W) and rf chuck power (250W). For NH$_3$-rich conditions (top) the etch rates for Ni and NiFeCo decrease with increasing pressure as recombination in the plasma becomes more important. For CO-rich conditions (bottom) there is a transition from deposition to etching, followed by the same decrease in etch rates at higher pressure. These results emphasize the importance of balancing ion flux and reactive neutral concentration in order to optimize the NiFe and NiFeCo etch rates in the CO/NH$_3$ plasma chemistry and may be an additional reason why most attempts in the past at using CO-based mixtures have been unsuccessful. Since there is a still a need to have a strong physical component to the etching, mask erosion (i.e. facetting leading to sloped sidewalls) is a problem when long etch times are needed. However for relatively shallow etch depths, mask erosion is less of an issue and quite impressive pattern transfer into NiFe (or NiFeCo) can be achieved with the CO/NH$_3$ mixture. Figure 6.17 shows SEM micrographs of features etched into NiFe using a 2CO/13NH$_3$, 750W source power, 250W rf chuck power, 2mTorr discharge. The sidewalls are smooth and vertical, but there is some rounding of the mask edges due to erosion during the plasma exposure.
Figure 6.1. Optical emission spectra from N$_2$, NH$_3$, CO/NH$_3$ and CO$_2$/NH$_3$ ICP discharges at fixed source power (1000W), rf chuck power (250W) and pressure (2mTorr).
Figure 6.2. Etch rates of NiFe and NiFeCo and selectivity to Al$_2$O$_3$ as a function of ICP source power in 2CO/13NH$_3$ (top) or 2CO$_2$/13NH$_3$ (bottom) discharges.
Figure 6.3. Etch rates of NiFe and NiFeCo as a function of source power (top) or rf chuck power (bottom) in ICP N\textsubscript{2}, Ar, CO/NH\textsubscript{3} discharges.
Figure 6.4. Etch rates of NiFe and deposited (D) or thermal (Th) SiO$_2$ as a function of either CO percentage (top) or process pressure (bottom) in ICP CO/NH$_3$ discharges.
Figure 6.5. Etch rates of NiFe and deposited (D) or thermal (Th) SiO$_2$ as a function of either ICP source power (top) or rf chuck power (bottom) in ICP CO/NH$_3$ discharges.
Figure 6.6. Etch rates of NiFe and deposited (D) or thermal (Th) SiO$_2$ as a function of substrate temperature in ICP CO/NH$_3$ discharges.
Figure 6.7. Etch rates of NiFe, NiFeCo, TaN, CrSi and Cu as a function of either ICP source power (top) or rf chuck power (bottom) in ICP CO/NH_3 discharges.
Figure 6.8. Etch selectivity for NiFe and NiFeCo over photoresist (top) or bias sputter deposited quartz (BSQ) as a function of either ICP source power (top) or rf chuck power (bottom) in ICP CO/NH$_3$ discharges.
Figure 6.9. SEM micrograph of features etched into a CrSi/NiFe/Cu/NiFeCo/TaN multilayer structure using an ICP CO/NH$_3$ discharge. The 3000Å thick SiO$_2$ mask is still in place.

Figure 6.10. SEM micrographs of features etched into a thick NiFe layer using an ICP CO/NH$_3$ discharge. The 5000Å thick SiO$_2$ mask is still in place, and little was lost on the field during the etch process.
Figure 6.11. Etch rates of NiFe and NiFeCo in CO/NH$_3$ (top) or CO$_2$/NH$_3$ (bottom) discharges (750W source power, 250W rf chuck power) as a function of plasma composition.
Figure 6.12. AES surface scans of NiFe before (top) and after (bottom) etching in 10CO/5NH$_3$ discharges (750W source power, 250W rf chuck power). The Si signal in the latter case comes from the edge of the sample where the substrate is exposed.
Figure 6.13. Optical emissions spectra of CO (top), Co$_2$ (center) or CO/NH$_3$ ECR discharges (1000W source power, 250W rf chuck power, 2mTorr).
Figure 6.14. Etch rates of NiFe and NiFeCo in 2CO/13NH$_3$ (top) or 10CO/5NH$_3$ (bottom) discharges (250W rf chuck power, 2mTorr) as a function of microwave source power.
Figure 6.15. Etch rates of NiFe and NiFeCo in 2CO/13NH\textsubscript{3} (top) or 10CO/5NH\textsubscript{3} (bottom) discharges (750W source power, 2mTorr) as a function of rf chuck power.
Figure 6.16. Etch rates of NiFe and NiFeCo in 2CO/13NH₃ (top) or 10CO/5NH₃ (bottom) discharges (750W source power, 250W rf chuck power) as a function of process pressure.
Figure 6.17. SEM micrographs of features etched into NiFe layers using a 2CO/13NH₃ discharge (750W source power, 250W rf chuck power, 2mTorr). The SiO₂ mask is still in place.
7. Vortex Matching

(Ivan K. Schuller, UCSD)

In continuations of our studies of vortex matching using artificially prepared magnetic structures we have performed studies on a variety of arrays which are distorted from simple symmetric systems. A particularly interesting study was the study of vortex matching using a rectangular array of pinning structures. In distinction to earlier studies of regular arrays, in these structures two vortex matching periodicities are present. One corresponds to a simple matching of an integer number of vortices per plaquette and the second periodicity corresponds to a distance ONLY along the motion of the vortices. In this fashion, a transition occurs in the vortex lattice from the situation in which there is a distortion to match the pinning array to a lattice which is matched only along one direction. This allows the first direct measurement of the elastic energy of the vortex lattice. We have also performed preliminary experiments using oxide superconductors. Several collaborations (with F. Sharifi, S. Pearton and S. Von Molnar) have been initiated on studies of artificially prepared ferromagnetic arrays on antiferromagnetic structures.
8. **Size Effects in Magnetic and Superconducting Materials**

*(R.C. Dynes)*

(a) **Superparamagnetic-Ferromagnetic Transfer**

We have studied the superparamagnetic-ferromagnetic transition of small Ni particles as a function of T and particle size. The transition has been detected in magnetoresistance and magnetization of thin discontinuous films of Ni quench-condensed on an insulating substrate. With increasing coupling between grains (=100Å in size) we observe a crossover from non-hysteric to hysteric behavior in from isolated grains to larger clusters. With increasing cluster size, the blocking temperature increases and the material becomes a ferromagnetic. This 2 dimensional crossover allows a study of the interactions between magnetic nanoparticles.

(b) **Micro SQUIDS**

We have developed the technology to manufacture micro SQUIDS to be used to study magnetic nanoparticles. We have fabricated SQUID loops ≈ 2 microns on a side using e-beam lithography techniques. The sensitivity of these SQUIDS is such that they are capable of detecting a single ferromagnetic nanoparticle (a few hundred angstroms in dimension) and will be used to study the switching characteristics of ferromagnetic particles. Attached is a Al SQUID.

(c) **Superconducting and Spin-Dependent Tunneling Using Native Oxide Barriers on CoFe Thin Films**

Spin dependent tunneling has been demonstrated in native oxide barriers of CoFe. Using a superconductor as a counter electrode it has been clearly demonstrated that the dominant conduction mechanism from CoFe to the superconductor is electron tunneling
through the native oxide. Replacing the superconductor with the ferromagnetic Co results in a magnetoresistance of \( \approx 4\% \). This is the largest value to date in a spin-dependent tunnel junction using a nature oxide barrier on a ferromagnet. Junction quality depends strongly on the deposition condition of the top electrode.
Figure 8.1  (a) Scanning Electron Microscopic picture of an Al SQUID (~2µm x 2µm loop size). The magnification is 22000x. On the right side of the quadratic loop there are two weak links which lead to a quantum interference.

(b) A typical $I_C$ versus $B$ pattern at $T=1.4K$. The modulation period is ~5 gauss, the critical current is about 40µA, with a modulation of about 2.5µA.
9. **Semiempirical SCF/CI Modeling of Ce$^{+3}$ 4f and 5d Energy Levels in Oxygen–doped Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4**

*(P. D. Rack and P. H. Holloway, UF)*

The alternating current thin film electroluminescent phosphors SrS:Ce and Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$:Ce have been found to emit blue light. It of interest to shift the color to a deeper blue and increase the emission efficiency to obtain a blue phosphor suitable for sunlight-readable full color displays. One promising approach is to co-dope with other ions, since the presence of other impurities in the host lattice can have an impact on both the energy and intensity of the Ce$^{+3}$ emission. For this reason we have studied the effect of the addition of oxygen to the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce phosphor, and find that the efficiency is nearly doubled and the Ce$^{+3}$ emission is shifted to a deeper blue.

The luminescent and structural properties of Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$:Ce were first studied by Peters and Baglio in 1972 and have more recently been investigated for electroluminescent display and field emission display phosphors. The Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$ host lattice was found to have a rather complex orthorhombic crystal structure, containing three slightly different M$^{+2}$ lattice sites (where M is Ca or Sr) with a concentration ratio of roughly 1:2:1. Ce$^{+3}$ ions substitute on M$^{+2}$ lattice sites. Recently, electron paramagnetic resonance (EPR) confirmed 3 different Ce$^{+3}$ sites in SrGa$_2$S$_4$ with the same 1:2:1 concentration ratio, suggesting that there is no preferential Ce$_M$ site in the lattice. Though the three different M$^{+2}$ sites differ slightly, they are all eight-fold coordinated with an antiprismatic symmetry (see Figure 9.1).

The results presented in reference are summarized here for convenience. Thin film Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce samples were rf magnetron sputter deposited from pressed powder targets. The films were doped with oxygen by backfilling with a mixture of argon and oxygen as the sputtering gas. X-ray photoelectron spectroscopy (XPS) confirmed oxygen incorporation.
Detailed analysis of the Ce 3d XPS peaks suggested that the added oxygen does interact directly with the Ce$^{3+}$ impurity, with on average three of the eight Ce-S bonds in the undoped samples replaced with Ce-O bonds in the oxygen doped samples. Figure 9.2 shows electroluminescence emission spectra for both an undoped and an oxygen-doped Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce thin film. A blue spectral shift of 15 nm (733 cm$^{-1}$) was observed when oxygen was introduced into the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce films. Both spectra show two peaks separated by about 45 nm (2063 cm$^{-1}$). The presence of two peaks is due to spin-orbit coupling, which splits the 4f orbital-derived $^2F$ state into $^2F_{7/2}$ and $^2F_{5/2}$ levels.

To understand the experimental observations we consider two properties of the host lattice that affect the luminescent center, the lattice symmetry and ion spacing. The former influences both the nature of the splitting pattern and, to a lesser extent, the magnitude of the splitting. In the present case oxygen and sulfur have the same valence state, so it is assumed that oxygen simply substitutes isoelectronically for sulfur, preserving the local symmetry of the luminescent center. The ion spacing affects both the Coulombic potential experienced by the valence electrons of the luminescent center, and the molecular orbital overlap with neighboring ions. Both effects are generally considered together as the ligand field strength, where it is understood that both increased Coulombic interaction and increased covalency (due to increased orbital overlap) increase the field strength.

In the case of the Ce$^{3+}$ 4f $\leftarrow$ 5d emission the Ce 4f orbitals are compact and shielded from the host lattice by the 5s and 5p electrons, and so are insensitive to the ligand field. The 5d orbitals are larger and not shielded and therefore their energy positions are sensitive to the host lattice. Since levels derived from the 4f orbitals are the lower levels involved in the emission spectroscopy, it is clear that the blue shift of the spectroscopy observed on the
addition of oxygen indicates a reduced ligand field affecting the 5d orbitals. This is graphically illustrated in Figure 9.3.

According to the spectrochemical series O\textsuperscript{2-} is considered a stronger-field ligand than S\textsuperscript{2-}. The spectrochemical series is based on ligand field splittings measured at the optimum metal-ligand distances found in isolated transition metal complexes, however, and the distance between Ce\textsuperscript{3+} and an O\textsuperscript{2-} ion \(r_{\text{CeO}}\) on a S\textsuperscript{2-} site is far greater than what would be found in a metal-oxygen complex. The large unrelaxed \(r_{\text{CeO}}\) leads to much smaller overlap of the oxygen orbitals with the cerium 5d orbitals, making O\textsuperscript{2-} a weaker-field ligand than S\textsuperscript{2-} in the absence of significant local lattice contraction. Certainly some lattice contraction is expected to accommodate the smaller O\textsuperscript{2-} ions, which would increase the overlap between oxygen valence orbitals and cerium 5d orbitals.

To investigate this we calculated overlaps of the cerium 5d orbitals with the valence orbitals of sulfur and oxygen at several distances using Slater-type atomic orbitals with radial exponents as given in references. The results show that at any Ce-O bond distance greater than 0.240 nm the total Ce-O overlap is smaller than the total Ce-S overlap at 0.300 nm (very close to the lattice spacing of SrS, 0.301 nm). It is doubtful that such a large distortion, on the order of 0.060 nm, would take place; the experimentally-observed blue shift indicates that it does not. The magnitude of the observed shift depends on an interplay between reduced covalency resulting from replacement of S\textsuperscript{2-} ions by O\textsuperscript{2-} ions and lattice contraction to accommodate the smaller ions.

To investigate the observed blue shift in the emission spectrum when oxygen was added to Ca\textsubscript{0.5}Sr\textsubscript{0.5}Ga\textsubscript{2}S\textsubscript{4}:Ce we performed semiempirical self-consistent field configuration
interaction calculations using the intermediate neglect of differential overlap Hamiltonian parameterized for spectroscopy, INDO/S, available in the ZINDO program package.

We use an embedded cluster model to treat a luminescent center (LC) in an extended ionic crystal lattice environment. The cluster consists of a small number of ions (including the LC) that are treated quantum-mechanically (“quantum ions”), and is embedded in a large array of Coulombic point charges constructed to provide the electrostatic effect of the bulk lattice on the quantum ions. Use of this approach with the INDO/S SCF/CI model has been shown to be effective in predicting the spectroscopy of the Ce$^{+3}$ LC in the host lattices MgS, CaS, SrS, and BaS. A detailed account of the computational approach is given there.

We use the octahedral SrS host lattice rather than the complex orthorhombic crystal structure of Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$ to model the effect of oxygen doping. This is a reasonable simplification because emission spectra of SrS:Ce and Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce are very similar, and we are interested in the change in transition energy caused by addition of oxygen rather than in absolute transition energies.

The cluster of quantum ions used to model the undoped SrS:Ce 4f and 5d-derived energy levels consists of thirteen ions. The Ce$^{+3}$ luminescent center was placed at the origin of a Cartesian axis system. Six S$^-$ ions were placed at $\pm a_0/2$ (0.301 nm) and six Sr$^{+2}$ ions were placed at $\pm a_0$ on the x, y, and z axes. This cluster was embedded in a 15x15x15 matrix of +2 and -2 point charges placed at the lattice positions of Sr$^{+2}$ and S$^-$ ions, respectively, to account for the electrostatic contribution of the rest of the host lattice. Point charges on faces, edges, and corners of the cubic array used are given appropriate fractional charges to obtain the proper Madelung potential at the origin.
The XPS measurements indicated an oxygen/sulfur ratio of 3/8 (0.375) in the first coordination sphere. Under the simplified octahedral lattice symmetry the closest O/S ratio is 2/6 (0.333), so to model the effect of oxygen doping we replace two $S^{2-}$ ions in the above cluster with $O^{2-}$ ions. Since some contraction of the Ce-O bond distance is expected, the calculations were performed at two relaxed Ce-O bond distances, 0.285 nm and 0.275 nm.

There are two possible symmetries of the central CeS$_4$O$_2$ cluster, $D_{4h}$ (with the oxygens on the $+z$ and $-z$ axes, for example) and $C_{2v}$ (with oxygens at $+z$ and $+x$, for example). Calculations were performed for both symmetries assuming a Ce-O distance of 0.285 nm. It was found that the total energies of the two clusters were very similar, differing by no more than 0.06 eV, and that the predicted spectroscopy was very similar as well. Thus we will present results at the two Ce-O bond distances assuming $D_{4h}$ cluster symmetry.

Cerium orbital energy level diagrams for the undoped $O_h$ cluster symmetry and the doped $D_{4h}$ cluster symmetry are shown in Figure 9.4. The final levels are indicated using the double-group notation of Bethe, and incorporate both spin-orbit and ligand field effects. In each symmetry the 4f orbitals are split primarily by spin-orbit coupling into $^2F_{7/2}$ and $^2F_{5/2}$ levels, by some 2000 cm$^{-1}$. These levels are themselves split by small amounts (on the order of 100 cm$^{-1}$) by the ligand field. The 5d orbitals are split primarily by the ligand field, into $^2T_{2g}$ and $^2E_g$ states in the case of $O_h$ symmetry, and further by smaller spin-orbit interactions. The latter amounts to about 1000 cm$^{-1}$ between $\Gamma_7(^2T_{2g})$ and $\Gamma_8(^2T_{2g})$. Finally, the energy difference between the ground $\Gamma_7(^2F_{5/2})$ level and $\Gamma_7(^2T_{2g})$ is on the order of 24000 cm$^{-1}$. Similar energies hold for the cluster with $D_{4h}$ symmetry. Figure 9.4 also shows the radiative transitions that give rise to the observed emission spectra. Calculated energies and oscillator
strengths for these transitions are given for the three clusters in table 1. In the table the transitions are numbered in order of increasing energy according to Figure 9.4.

The experimentally-observed Ce$^{3+}$ emission bands are convolutions of the various transitions indicated in Figure 9.4 and accompanying vibronic transitions. As discussed in reference, transition energies computed using the INDO/S SCF/CI model represent band maxima of absorption processes. Band maxima of the corresponding emission processes are shifted to lower energy, since emission maxima are typically lower in energy than the 0-0 phonon line while absorption maxima are at higher energy than the 0-0 phonon line, see Figure 9.5. This so-called Stokes shift (denoted by $\Delta E$ in the figure) can be as large as 0.25 – 0.50 eV. The phosphors under question are very similar, so $\Delta E$ should be more or less constant. Given that, no explicit account of $\Delta E$ is made since we are interested in relative rather than absolute transition energies.

An approximate vibronic spectrum can be fit from the calculated transition energies and intensities by fitting each transition with a Gaussian curve having a fixed full-width-at-half-maximum and an integrated area equal to the calculated oscillator strength. Figure 9.6 shows approximate emission spectra generated in this way for SrS:Ce and oxygen-doped SrS:Ce with Ce-O bond distances of 0.285 nm and 0.275 nm. The asymmetric bimodal distribution observed in the experimental spectra (see Figure 9.2) is clearly reproduced, as is the blue shift caused by addition of oxygen to Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce. $\Delta E$ (Figure 9.5) is obvious when comparing the approximate spectra in Figure 9.6 with the experimental spectra in Figure 9.2, and appears to be on the order of 3000 cm$^{-1}$ (0.37 eV).

Quantitatively the blue shift in the energy of the band maximum of the high energy component of the 4f-5d emission spectrum is found to be 1470 cm$^{-1}$ for $r_{\text{CeO}} = 0.285$ nm and
960 cm$^{-1}$ for $r_{\text{CeO}} = 0.275$ nm. These results are in good agreement with the experimentally observed blue shift of 733 cm$^{-1}$, given that we have guessed at geometric distortions and have used an octahedral lattice rather than an orthorhombic one. The fact that the predicted blue shift is smaller at $r_{\text{CeO}} = 0.275$ nm suggests that the energy shift is caused by changes in covalency experienced by the Ce 5d orbitals since there is an opposing crystal field effect when the lattice contracts.

The SCF/CI results provide atomic orbital populations that are a quantitative indication of covalency. To demonstrate that decreases in covalency blue shift the spectroscopic transitions, occupations of the Ce 5d orbitals in the Ce$^{3+}$ ground 4f$^1$ state were calculated for the three cases (undoped, doped with $r_{\text{CeO}} = 0.285$ nm, doped with $r_{\text{CeO}} = 0.275$ nm) and are shown in table 2. The Ce$^{3+}$ ion has the electron configuration [Xe]4f$^1$5d$^0$ in its ground state, so if the interaction of the 5d orbitals and the neighboring S$^{2-}$ ions was purely ionic these populations would be zero. Covalent overlap with the filled orbitals of S$^{2-}$, on the other hand, would cause a small amount of electrons to occupy the 5d orbitals. The total occupation of the cerium 5d orbitals is then a measure of the extent of covalency. As shown in table 2 the trend in populations shows that the spectroscopic shifts do follow changes in covalency caused by the smaller overlap of the oxygen orbitals with the Ce 5d orbitals.

The efficiency of the Ce$^{3+}$ 4f-5d emission was nearly doubled by addition of oxygen to the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce phosphor. This is not reflected by the total oscillator strengths predicted for the three model clusters (table 1), indicating that a change in some property other than the intrinsic brightness of the transitions is responsible for the increase in efficiency observed in the electroluminescence. Possibilities include an enhancement of the rate of injection of electrons into the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$ film caused by changes at the
phosphor/insulator interface, or an increase in the luminescent center cross-section due to the presence of oxygen ions in the immediate vicinity of Ce$^{3+}$.

The trend in the total oscillator strengths calculated for the three model clusters is easily understood in terms of the cluster symmetries. Replacement of sulfur ions by oxygen ions relax the formal octahedral symmetry of the undoped cluster, causing the increase in intensity predicted for the doped clusters. When comparing the two doped model clusters, it is apparent that the departure from octahedral symmetry is more pronounced for the longer value of $r_{\text{CeO}}$ since the orbital overlap decreases as $r_{\text{CeO}}$ increases, causing the total oscillator strength to be larger for the model cluster with larger $r_{\text{CeO}}$.

Semiempirical SCF/CI calculations utilizing an embedded cluster model with octahedral symmetry found an increase in 5d-4f transition energies when two sulfur ions were replaced with oxygen ions. Quantitatively, an oxygen to anion ratio of 0.333 (2/6) increased the energy of the band maximum of the blue component of the 5d-4f emission spectrum by 1470 cm$^{-1}$ for a Ce-O bond distance of 0.285 nm and by 960 cm$^{-1}$ for a Ce-O bond distance of 0.275 nm. The calculated shifts are in good agreement with the experimentally determined shift of $\sim 730$ cm$^{-1}$ that was observed upon addition of oxygen to the Ca$_{0.5}$Sr$_{0.5}$Ga$_2$S$_4$:Ce phosphor. An atomic orbital electron population analysis revealed that the experimentally-observed blue shift is due to a decrease in the covalent character of the Ce 5d orbitals upon addition of the smaller O$^2-$ ions on S$^2-$ sites. Computed oscillator strengths indicate that the large increase observed in the efficiency of electroluminescence caused by addition of oxygen is not due to a change in the inherent brightness of the emission.
Table 1. Calculated Ce 4f-5d transition energies and oscillator strengths for undoped SrS:Ce and oxygen doped SrS:Ce with $r_{\text{CeO}}$ of 0.285 nm and 0.275 nm.

<table>
<thead>
<tr>
<th>Transition (Figure 9.4)</th>
<th>Undoped SrS:Ce</th>
<th>Doped, $r_{\text{CeO}}$ 0.275 nm</th>
<th>$r_{\text{CeO}}$ 0.285 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21010</td>
<td>0.0268</td>
<td>21930</td>
</tr>
<tr>
<td>2</td>
<td>21040</td>
<td>0.0528</td>
<td>21960</td>
</tr>
<tr>
<td>3</td>
<td>21050</td>
<td>0.0032</td>
<td>22000</td>
</tr>
<tr>
<td>4</td>
<td>23190</td>
<td>0.0986</td>
<td>22020</td>
</tr>
<tr>
<td>5</td>
<td>23220</td>
<td>0.0566</td>
<td>24120</td>
</tr>
<tr>
<td>6</td>
<td>--</td>
<td>--</td>
<td>24130</td>
</tr>
<tr>
<td>7</td>
<td>--</td>
<td>--</td>
<td>24190</td>
</tr>
<tr>
<td>Total</td>
<td>--</td>
<td>0.2389</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 2. Ce 5d atomic orbital electron populations calculated for SrS:Ce and oxygen doped SrS:Ce with $r_{\text{CeO}}$ of 0.285 nm and 0.275 nm, and energies of the corresponding band maxima. If the interaction was purely ionic the population would be zero.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Total Ce 5d orbital electron population</th>
<th>Energy of band maximum (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped SrS:Ce</td>
<td>1.63</td>
<td>23190</td>
</tr>
<tr>
<td>Oxygen doped, $r_{\text{CeO}}$ 0.275 nm</td>
<td>1.58</td>
<td>24150</td>
</tr>
<tr>
<td>Oxygen doped, $r_{\text{CeO}}$ 0.285 nm</td>
<td>1.55</td>
<td>24660</td>
</tr>
</tbody>
</table>
Figure 9.1. Antiprismatic symmetry of the Ce$^{3+}$ site in Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$:Ce. Shown are the Ce$^{3+}$ ion (center) and the eight nearest-neighbor sulfur ions.

Figure 9.2. Electroluminescent emission spectra of undoped and oxygen-doped Ca$_x$Sr$_{1-x}$Ga$_2$S$_4$:Ce thin films.

Figure 9.3. Energy level diagram showing how an observed blue shift in Ce$^{3+}$ 4f-5d emission results from a decrease in the ligand field strength. Energy differences between levels are not to scale, and are described in the text.
Figure 9.4. Energy level diagrams for Ce\(^{+3}\) under a) octahedral symmetry and b) D\(_{4h}\) symmetry along with the radiative transitions giving rise to the emission spectrum for each.

Figure 9.5. Schematic representation of absorption and emission bands displaying Stokes shift between band maxima.

Figure 9.6. Calculated spectra of undoped SrS:Ce and oxygen doped SrS:Ce with \(r_{\text{CeO}}\) of 0.285 nm and 0.275 nm.
10. Magnetoresistance and Magnetic Properties of Lanthanum Manganite Films

(R.K. Singh, UF)

In this report we present our studies on the magnetoresistance (MR) behavior and magnetic properties of La$_{1-x-y}$Ca$_x$MnO$_3$ system in thin film form. By varying the values of $x$ and $y$ in La$_{1-x-y}$Ca$_x$MnO$_3$, we have synthesized an external ($x = 0.3$, $y = 0$), an internal ($x = 0$, $y = 0.3$) and a mixed doped ($x = 0.2$, $y = 0.1$) system with same Mn$^{3+}$/Mn$^{4+}$ ratio. Thin films of these materials have been grown in situ on (100) LaAlO$_3$ substrates using a pulsed laser deposition technique. XRD patterns of La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$Ca$_{0.2}$MnO$_3$ and La$_{0.7}$MnO$_3$ films are shown in Figure 10.1. The films were grown on (100) LaAlO$_3$ substrates at 700 °C and were 1000 Å thick. According to XRD patterns, all the films are single phase with (00$l$) peaks with $l = 1$ and 2. The presence of only (00$l$) peaks implies the highly textured growth of all the films on (100) LaAlO$_3$ substrate. The lattice parameters of La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$Ca$_{0.2}$MnO$_3$ and La$_{0.7}$MnO$_3$ films were found to be 3.87, 3.91 and 3.90 Å, respectively. Figure 3 shows the AFM micrographs of these films. The root mean square (rms) roughnesses of the films measured using AFM were found to be 1.425 nm, 3.17 nm and 5.83 nm respectively. The value of rms roughness obtained suggests that as-deposited manganite thin films in the present study are very smooth and the roughness observed is sometimes similar to the roughness of the bare substrate surface.

The variation of electrical resistance in zero and applied field (5T) as a function of temperature for La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$Ca$_{0.2}$MnO$_3$ and La$_{0.7}$MnO$_3$ films are shown in Figure 10.2. All the three films were grown under identical conditions so that film thickness and oxygen contents of all the films could be kept identical. According to the variation of
resistance shown in Figure 10.2, all the three films have similar qualitative magnetotransport behavior. That is, all the films undergo an insulator to metal (I-M) transition as the temperature is lowered down and the resistance of all the films is suppressed significantly with the application of magnetic field. However, the temperature at which I-M transition takes place in each system is different from each other. The internal doped system (La$_{0.7}$MnO$_3$) attains the metallic state earliest (240 K) followed by the mixed doped system (La$_{0.7}$Ca$_{0.2}$MnO$_3$), and external doped (La$_{0.7}$Ca$_{0.3}$MnO$_3$) system with insulator to around 220 and 200 K, respectively. Thus, it appears that the electronic doping in self-doped compounds is similar to that of the compounds with external doping.

The difference in the values of I-M transition temperature in these systems may be explained on the basis of tolerance factor ($t$). The tolerance factor essentially determines the Mn-O-Mn bond angle, which in turn, controls the effective electron transfer between Mn$^{3+}$ and Mn$^{4+}$ within the framework of double exchange mechanism. The deviation in $t$ from unity is a measure of the mismatch between the equilibrium bond lengths La-O and Mn-O in a perovskite structured lanthanum manganite system. The room-temperature, ambient-pressure value of $t$ is calculated from the sums of the empirical ionic radii. A $t<1$ places the Mn-O bonds under compression and La-O bonds under tension. If these internal stresses are not relieved due to structural hindrance in rotation of MnO$_6$ octahedra, the lattice will be in the state of internal pressure. The tolerance factors of the compounds investigated in the present study, La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$Ca$_{0.2}$MnO$_3$ and La$_{0.7}$MnO$_3$, were calculated to be 0.90, 0.85, and 0.80, respectively. Therefore, these compounds with varying tolerance factors are likely to experience different internal stresses, and hence, different chemical pressures. As a result of difference in chemical pressure, the insulator to metal transition in each system
occurs at different temperature: $\text{La}_{0.7}\text{MnO}_3$ films which has largest deviation of $t$ from unity, and hence, highest internal chemical pressure undergoes an I-M transition at higher temperature (240 K) compared to I-M transitions of $\text{La}_{0.7}\text{Ca}_{0.2}\text{MnO}_3$ (I-M transition: 220 K) and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (I-M transition: 200 K) films.

The MR ratios of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, $\text{La}_{0.7}\text{Ca}_{0.2}\text{MnO}_3$ and $\text{La}_{0.7}\text{MnO}_3$ films were calculated using the data in Figure 10.2. The MR ratios obtained are plotted in Figure 10.3 as a function of temperature at 5 T. The figure shows that $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ has the highest MR ratio (~825%) which is followed by $\text{La}_{0.7}\text{Ca}_{0.2}\text{MnO}_3$ (MR ratio ~750%) and $\text{La}_{0.7}\text{MnO}_3$ (MR ratio ~700%) systems. The variation in MR ratios of these compounds are explained as follows. The occupancy of $e_g$ band is expected to be similar for all the three systems assuming that oxygen remains divalent and Mn$^{3+}$/Mn$^{4+}$ ratio is the same in all the systems. However, due to difference in vacancies at La-sites (arising from lanthanum deficiency), the localization effects, and hence, the mobility of charge carriers are different in different systems. Since the density of lanthanum deficiency is more in $\text{La}_{0.7}\text{MnO}_3$ system (internal doped), the localizing effect of random vacancies is stronger in $\text{La}_{0.7}\text{MnO}_3$ films than that in $\text{La}_{0.7}\text{Ca}_{0.2}\text{MnO}_3$ (mixed doped) film. Therefore, the random potential fluctuations due to missing La$^{3+}$ ions will favor the Anderson localization more strongly in the former system than in the later system. As a result of this, the MR ratio obtained for $\text{La}_{0.7}\text{MnO}_3$ film is less than that of $\text{La}_{0.7}\text{Ca}_{0.2}\text{MnO}_3$ film. There is no such localization effect in stoichiometric $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films due to absence of vacancies which is manifested with the realization of highest MR ratio among the three systems discussed here.

To understand the nature of transport phenomena in each film, we have analyzed low temperature resistance for all the three films using a polynomial expansion in temperature
As shown in Figure 10.4, resistances of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.2}$MnO$_3$ films are fit well by the equation: \( R = R_0 + R_1 T^2 \), whereas the resistance of La$_{0.7}$MnO$_3$ film is fit well by equation: \( R = R_0 + R_1 T^{2.5} \) for temperatures less than \( T_c/2 \). Here, \( T_c \) is paramagnetic to ferromagnetic transition temperature and \( R_0 \) is the residual resistance. \( R_1 T^{2.5} \) fit suggests a combination of electron-electron, electron-phonon, and electron-magnon scattering (observed in case of La$_{0.7}$MnO$_3$), while \( R_1 T^2 \) fits suggest an electron-electron scattering (observed in La$_{0.7}$Ca$_{0.2}$MnO$_3$ and La$_{0.7}$Ca$_{0.3}$MnO$_3$).

In the regime above \( T_c \), resistance of all the three systems closely follows the law predicted by small polaron hopping: \( \ln(R/T) = \ln(R_h) + E_a/k_B T \), as opposed to that predicted for a semiconductor: \( \ln(R) \propto 1/T \) (Fig. 5). Therefore, we conclude that the temperature dependence of the resistance is due to the temperature dependence of mobility while the carrier concentration remains constant.

In summary, we have reported our studies on the microstructure, magnetoresistance and magnetic properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7}$MnO$_3$, and La$_{0.7}$Ca$_{0.2}$MnO$_3$, which represent external, internal, and mixed doped systems with the same Mn$^{3+}$/Mn$^{4+}$ ratio. The results obtained have shown that the electronic doping in non-stoichiometric compounds is similar to that of the compounds with divalent substitution. The variation in insulator to metal transition and MR ratio in these systems have been explained using the concept of internal chemical pressure and localization effects. Analysis of low temperature resistance has shown that in La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.7}$Ca$_{0.2}$MnO$_3$ electron-electron scattering dominates while in La$_{0.7}$MnO$_3$ a combination of electron-electron, electron-phonon and electron-magnon scattering dominates. High temperature resistance is consistent with small polaron hopping conductivity for all the three systems.
Figure 10.1. X-ray diffraction patterns of (a) La$_{0.7}$Ca$_{0.3}$MnO$_3$, (b) La$_{0.7}$Ca$_{0.2}$MnO$_3$ and (c) La$_{0.7}$MnO$_3$ films grown at 700$^\circ$C on (100) LaAlO$_3$ substrates.
Figure 10.2  Resistance versus temperature plots (a) La$_{0.7}$MnO$_3$, (b) La$_{0.7}$Ca$_{0.2}$MnO$_3$ (c) and La$_{0.7}$Ca$_{0.3}$MnO$_3$ films at 0 and 5 T magnetic field.
Figure 10.3  Variation of MR ratio with temperature for La$_{0.7}$MnO$_3$ (filled square), La$_{0.7}$Ca$_{0.2}$MnO$_3$ (filled triangle) and La$_{0.7}$Ca$_{0.3}$MnO$_3$ (filled circle).
Figure 10.4. Low Temperature (below $T_c/2$) resistance fits for La$_{0.7}$Ca$_{0.3}$MnO$_3$ (filled circle), La$_{0.7}$Ca$_{0.2}$MnO$_3$ (filled triangle) and La$_{0.7}$MnO$_3$ (inset) at 0 and 5T.

Figure 10.5. High temperature fits for for La$_{0.7}$Ca$_{0.3}$MnO$_3$(circle), La$_{0.7}$Ca$_{0.2}$MnO$_3$ (triangle) and La$_{0.7}$MnO$_3$ (square).
11. Nanofabrication

(Fred Sharifi, UF)

Over the course of the past reporting period, our research effort has concentrated on three separate areas involving fabrication and fundamental studies of GMR-based structures.


We have developed a growth process for fabrication of GMR structures where the low field sensitivity of the multilayer is enhanced significantly compared to normally grown structures. Prior to the growth, the substrates are exposed to a Xe ion plasma, decreasing the surface mobility of the deposited film. The process leads to smoother films at lower thickness and removes the need for buffer layers. Our initial results show an improvement of over one order of magnitude in low-field sensitivity of these films compared to identical films grown without the plasma-processing step.

11.2 Development of resist-less processing methods for fabrication of GMR-based MRAM cells and interconnects.

We have fabricated a series of stencil deposition masks made from 200 nm thick Si$_3$N$_4$ membranes patterned in geometries appropriate for MRAM cells and interconnects. These membranes are thin enough to allow for in-situ deposition of MRAM stacks and remove the need for post-deposition patterning. The masks are robust and stable, and can be used for multiple depositions. We are currently exploring the limits on pattern density that can be achieved using this technique and methods for improving the reliability of the mask so as to make the technique viable for industrial applications.
11.3 Studies of one-dimensional GMR wires.

We are currently engaged in a series of comprehensive magneto-transport measurements on wires with lateral sizes less than 100 nm made of Cu/Co GMR multilayers. The goal of these measurements is to see whether the GMR ratio in such structures is dependent on the lateral wire dimensions. Our preliminary results show a small enhancement of the GMR ratio in these wires compared to two-dimensional films fabricated under identical conditions. Our final goal is to ascertain whether these nanowires will lead to a significant enhancement of magnetoresistance and whether they are viable as sensors and detectors.
12. Carbon Nanotube Modified Cantilevers for Improved Spatial Resolution in Electrostatic Force Microscopy

(S. B. Arnason, A. R. Rinzler, Q. Hudspeth and A. F. Hebard, UF)

Variations of scanning force microscopy (SFM) techniques are presently attracting serious research attention because of their ability to uniquely characterize the electrical properties of surfaces and interfaces. In contrast to scanning tunneling microscopy (STM), which offers atomic scale spatial resolution only on conducting surfaces, the SFM techniques can be used on a wide variety of surfaces consisting of insulating, conducting, and/or semi-conducting components. All of the SFM techniques require a conducting tip so that a potential difference can be applied between the tip and substrate. In non-contact mode, electrostatic forces that act on a conducting tip oscillating above the substrate surface are sensed. High-resolution capacitance detection and Kelvin probe force microscopy can detect capacitances on the order of 10^-19 farad and forces on the order of 100pN. Measurements using these electrostatic force microscopy (EFM) techniques include contact electrification studies, high-resolution imaging of contact potential differences on Au covered Si(111) surfaces, dopant profiling in silicon, imaging of potential drops on integrated circuit chips, and imaging of the conducting and non-conducting regions of carbon-insulator and thin-film silver systems near the percolation threshold.

In any scanning probe technique the nature of the probe tip can make a significant if not critical impact on image quality. The report by Dai et al. on the use of multi-walled carbon nanotubes (MWNT's) attached directly onto conventional silicon cantilevers signaled a major advance for SFM techniques. A major advantage is that a nanotube is robust yet flexible enough to survive repeated tip crashes. The typical diameter of the tip end is on the order of 5-20nm, thus allowing high resolution imaging of surface topography. In addition
its slender pencil-like shape enables it to probe and image deep recesses in surface topography. More importantly for EFM applications the MWNT's are conducting thus allowing for the placement of a small-area conducting probe in close proximity to the surface under investigation. A less obvious but equally important aspect of nanotube tips for EFM applications is that the elongated pencil-like shape of the nanotube (as an extension to the cantilever) minimizes the capacitance between the cantilever and the substrate and thus reduces gradients in the capacitance. The results here illustrate this advantage and show that significant improvements in EFM imaging are obtained with the use of nanotube-modified cantilevers.

A straightforward analysis of EFM operation, depicted schematically in Figure 12.1, reveals the effect of capacitative coupling. The electrostatic force on a conducting tip held a distance $z$ above a conducting surface is

$$F = -\frac{V^2}{2} \frac{\partial C}{\partial z}$$

where $V$ and $C/z$ are respectively the potential and the gradient of the capacitance between the tip and the substrate. The potential difference, $V = V_S - V_{dc} + V_{ac}\sin(t)$, comprises three contributions, an intrinsic term associated with nonuniform charge distributions and/or variations in surface work function together with an extrinsic contribution arising from externally applied dc and ac terms. The force modulation appearing at the applied frequency (has an amplitude proportional to the product $(V_S - V_{dc})V_{ac}C/z$ which can be conveniently driven to zero when $V_{dc}$ is set to the unknown surface potential $V_S$.

A Park CP AutoProbe SPM was used for the simultaneous acquisition of topographical and EFM images. The cantilever is driven into oscillation just above its
resonant frequency (>100kHz) and the demodulated signal fed back to the scanning stage to maintain a pre-set oscillation amplitude. In this non-contact mode topographical images are obtained without shorting the tip to the substrate. An additional feedback circuit, shown in Figure 12.1 was used for the EFM image. An electric potential applied at a significantly lower frequency, /2=20kHz, produces a force modulation that is continuously nulled by the feedback circuit [Weaver]. It is straightforward to show that the output voltage of the lock-in amplifier in Figure 12.1 can be written as

\[ V_{out} = V_s \frac{(G/2)V_{AC} \frac{\partial C}{\partial z}}{1 + (G/2)V_{AC} \frac{\partial C}{\partial z}} \]

where \( G \) is the overall gain of the circuit. When \( G \) is large, then \( V_{out} (=V_s) \) becomes a direct measure of the surface potential and is used as the source for the simultaneously acquired EFM image.

In practice too much gain will induce oscillations and/or instabilities, and one must accept a limited gain to obtain a stable EFM image. The amount of gain that is compromised depends on a variety of factors including scan speed, surface roughness, and the size of the variations in \( V_s \). Consequently, as seen from Eq. 3, topographical features relating to the spatial variation of \( C(x,y)/z \) will appear in the EFM image. As will be shown below, nanotube modified tips minimize the contribution from \( C(x,y)/z \) and thus help to separate topographical from electrostatic features. This is accomplished primarily because the nanotube extension places the silicon tip of the cantilever further from the substrate thus diminishing the capacitance between the main body of the cantilever and the substrate. More importantly, the pencil-shaped nanotube presents a uniformly narrow cylindrical cross sections which, when convolved with topographical variations, gives optimal resolution with minimal broadening. This advantage has already been demonstrated for topographical imaging of trenches with steep sidewalls [Dai].
All of the measurements presented in this paper are made on Al-Al2O3-Al cross-stripe tunnel junctions (see Figure 12.1 inset). By applying a dc voltage bias to a vertically structured tunnel junction with sharply defined edges, a calibrated step function change in surface voltage and topograph will simultaneously occur as the tip is scanned across the junction electrodes. This configuration thus allows a meaningful comparison of the suitability of various types of tips in acquiring topographical and EFM images. The junctions are fabricated using standard photolithographic techniques to define the stripes. First an initial layer of 300Å-thick Al is deposited from a thermal evaporation source onto a glass substrate. Without breaking vacuum the surface of the Al is oxidized in a dc plasma discharge in 50mTorr of oxygen. The sample is removed from the vacuum system and the base electrode defined by lift off. Photoresist is spun onto the resulting sample and patterned to allow the formation of the counter electrode. The sample is reinserted into the vacuum system and another 300Å of Al deposited. Again, liftoff defines the top electrode.

Figures 12.2 and 12.3 represent simultaneously acquired topographical (left panel) and electrostatic voltage scans (right panel) in the vicinity of the tunnel junction boundary using a conventional silicon tip (Figure 12.2) and a nanotube-modified tip (Figure 12.3). The labels S, B, and T refer respectively to the substrate, the base electrode, and the top electrode. These images are taken with 20 mV of bias between top and bottom plates, 200 mV of bias on the sample relative to ground, and 500 mV of AC bias on the scanning probe at a frequency of 20 kHz. In the voltage micrograph taken with a conventional tip (Figure 12.2) there is a strong signal from the capacitance gradient as the tip climbs from the portion of the top electrode that is on the substrate, T1, to that portion which covers the bottom electrode, T2. This manifests itself as a diffuse bright area at the edge. By contrast, the edges in the
image acquired with a nanotube-modified tip show significantly smaller capacitance gradient
effects, clearly resolving the step edges. In both of these figures the voltage drop between the
electrodes is measured to be 20+/−5 mV, equivalent to the applied bias.

Figure 12.4 represents the simultaneously acquired topographical (left panel) and
electrostatic voltage (right panel) scans acquired with a nanotube modified tip of a bundle of
multiwalled nanotubes resting on the oxidized surface of an aluminum cross stripe. The
image is taken with an AC bias of 2V applied at 20 kHz. This sample has no applied DC bias
so the resulting potential image represents solely the surface contact potential of the tubes.
The topograph shows a complex tangle of tubes, some of which stretch horizontally across
the image, others start vertical and bend to the right at the image center. The potential image
presents a distinct picture. Some of the tubes appear to have their potentials pinned to that of
the substrate, while others are at a clearly different potential. The lower frame of figure 4
shows the potential as a function of distance along the line drawn across the lower extension
of the main feature in the potential image. From this line trace we can see that these tubes sit
at a potential 15-20 mV below that of the substrate, that features with depths of 5 mV are
clearly resolvable and that the spatial resolution possible with the nanotube modified tip is 10
nm. In the box in the lower right hand corner of the potential image the RMS voltage is
measured to be less than 1mV, this is an approximate measure of the noise in our signal.

In conclusion, we have been able to use the advantageous physical properties of
nanotube modified scanning probe tips to improve the spatial and voltage resolution of our
EFM micrographs taken in a scanning kelvin probe configuration. The high aspect ratio of
the nanotubes removes the topographical variation in the capacitance gradients which can
cause topography to adversely couple into the EFM images. In addition, these tips are robust
and consistent, producing excellent images over months of use in the best cases. This is to be contrasted with our standard tips, which lose spatial resolution with wear and have changing electrical properties as the result of contamination. As a result of these improved properties we are able to make measurement of the relative surface contact potential of multiwalled nanotubes.
Figure 12.1. Schematic representation of the circuit. The output of the lock-in is summed with the AC bias in feedback to null the first harmonic signal. In general two independent bias voltages are applied to the two legs of the tunnel junction.
Figure 12.2. Simultaneously acquired topography (left frame) and potential (right frame) micrographs of an Al-Al\(_2\)O\(_3\)-Al tunnel junction biased at 200 mV with respect to ground with 20 mV of relative bias between electrodes, imaged with a conventional Si tip. Note the topographic enhancement of the potential signal at the step edges, particularly at the edge between the portions of the top electrode on the substrate and over the bottom electrode, \(T_1\) and \(T_2\), which are at a common potential.
Figure 12.3. Images analogous to those in Figure 2, acquired with a nanotube modified tip. Note that potential bias is reversed relative to Figure 2. All of the edges in this potential image have significantly less edge enhancement of the EFM signal. In addition the spatial resolution is significantly improved.
Figure 12.4. Topography (left frame) and surface contact potential (right frame) of a bundle of nanotubes resting on the oxidized surface of an Aluminum electrode. While some of the tube potentials match that of the aluminum oxide surface, others sit 20 mV below this level. The bottom frame shows a line trace of a cut through the lower portion of the central feature (the placement of the cut is shown schematically as a line on the potential micrograph). The RMS voltage variation of the potential in the box in the lower right hand corner is less than 1 mV.
13. **Ion Beam Sputter Deposition of GMR Materials**

*(D. Temple, MCNC in collaboration with A.F. Hebard and F. Sharifi, UF)*

I. **Summary**

**MCNC’s Role in the Program**

During the last year, the project at MCNC was guided by the following objectives:

- Demonstrate deposition of magnetic multilayers exhibiting the giant magnetoresistive (GMR) effect using the ion beam sputter deposition (IBSD) system designed, constructed, and automated in-house.

- Investigate effects of IBSD process parameters on the GMR ratio; these parameters include energy of the primary ion beam and the type of ions.

In addition, MCNC program objectives included providing support for development of magnetic materials at the University of Florida and other organizations participating in the MURI program through:

- design of lithographic masks/reticles for use in patterning of magnetic materials;

- providing wafers with high-resolution liftoff patterns for deposition of magnetic films and multilayers.

**Progress During the Last Reporting Period**

- Demonstrated deposition of Fe/Cr multilayers exhibiting the GMR effect. The maximum value of GMR obtained so far was 25% at 10K which is, for the Cr spacer thickness layer chosen, comparable to the best values reported for polycrystalline Fe/Cr multilayers deposited by magnetron sputtering. The optimization process is in progress, so further increase of the GMR value is likely.
• Conducted investigations of effects of the primary ion beam energy and the type of ions on magnetic and magnetoresistive properties of Fe/Cr multilayers. Best results so far have been obtained using Xe ions at 900 eV. Examination of the effects of lowering the primary beam energy for both Xe and Ar ions is in progress. Preliminary results indicate that, as long as the films remain free of impurities (as evidenced by e.g. unchanged film resistivity values), lower beam energies result in increased GMR ratios. Simulations of energy distributions of sputtered atoms, as well as backscattered working gas atoms (neutrals), were conducted using the SRIM software to understand effects of the IBSD process conditions on the parameters affecting the film growth.

• Several batches of wafers with high-resolution liftoff photoresist patterns were delivered to the University of Florida; some of these wafers were used for preparation of samples for studies of mechanical properties of microwires conducted at the Naval Research Laboratory. The high-resolution liftoff process, developed at MCNC in the framework of the MURI program, is described in detail in previous reports (#1 and #2).

• Two sets of photolithographic masks were designed and fabricated for the University of Florida.

II. Detailed Description - Ion Beam Sputter Deposition Development

II.1. Motivation

Metal multilayer films exhibiting the GMR effect are typically deposited using magnetron sputtering or molecular beam epitaxy (MBE) methods. IBSD is an alternative technique that has recently attracted attention. The strengths of this technique include uniform deposition, reproducibility, and elimination of stray fields at the substrate. On a more basic level, the ion
beam sputter deposition technique is unique in that it provides control over many of the fundamental properties of sputtered atoms that affect the film growth. Because of the nature of the ion source and flexibility in relative positioning of the source, targets, and the substrate, the flux of sputtered atoms and the energy and angular distributions of the atoms, as well as energetic particle bombardment of the growing film, can be independently controlled. This is quite different from a typical planar magnetron configuration where changing a process variable, such as cathode power or chamber pressure, affects several of these growth parameters simultaneously.

In spite of these advantages, only a few studies have been published regarding properties of IBSD GMR structures (primarily spin valves), and little information is available on the effects of the controllable parameters of the deposition process on magnetic and magnetoresistive properties of the films. We have chosen Fe/Cr multilayers composed of 30 periods as the first test case. There have been numerous reports in the literature regarding Fe/Cr multilayers deposited using either magnetron sputtering or MBE techniques. These provide a reference for comparison with films deposited as part of this program. To our knowledge, there have been no reports on properties of Fe/Cr multilayers deposited by IBSD. The knowledge acquired during the optimization of the Fe/Cr multilayer deposition process will be applied to other material systems, such as Co/Cu and NiFe/Cu.

II.2. Fe/Cr Multilayers Deposited with Argon Ion Beams

All investigated films were deposited in the IBSD system, which had been designed, constructed and automated in-house, as described in detail in a previous progress report (#3). The system incorporates an RF ion gun and a rotating carousel with room for four targets. Each of the targets can be rotated during deposition. Targets can also be tilted with respect to
the incoming ion beam. Loading and unloading of samples in and out of the deposition chamber is achieved through a turbo-pumped load lock. The samples are typically 4-inch Si wafers but wafers up to 6 inches in diameter can be accommodated. The substrate holder is equipped with a heater which has been tested at temperatures up to 400°C. The ion gun operation, substrate rotation and target rotation systems are interfaced to a LabView computer program.

Deposited multilayers are characterized using transmission electron microscopy (TEM), atomic force microscopy (AFM), Auger electron spectroscopy (AES), as well as resistivity, magnetic hysteresis loop and magnetotransport measurements. Film resistivity is determined from sheet resistance values, obtained using a four-point probe. Magnetic hysteresis loop measurements are performed using a vibrating sample magnetometer (VSM). Magnetotransport measurements have been obtained at the University of Florida (in the group of Dr. Arthur Hebard, one of the investigators in the MURI program) using two different instruments. The first of these, a Physical Properties Measurement System (PPMS, Quantum Design) allows measurements as a function of temperature (2-400K), magnetic field (0-7T), and angle (0-360 degrees). The second instrument, a Magnetic Properties Measurement System (MPMS, Quantum Design), can also be used for magnetoresistance measurements. Its temperature and field ranges are similar to those of the PPMS.

Fe/Cr multilayer films deposited in the early stage of the development program, described in the previous progress report (#3), exhibited relatively modest GMR ratios (on the order of a few %) and only a partial antiferromagnetic alignment of the Fe layers, as was evidenced by a large remanent magnetic moment visible in magnetic hysteresis curves. This partial alignment was attributed to pinholes in Cr spacers providing channels for physical
coupling of adjacent ferromagnetic Fe films. Several changes were implemented following these preliminary results. The position of the ion gun in the IBSD chamber was changed with respect to the target carousel; the pumping package was upgraded by adding a high vacuum cryogenic pump, thus lowering the base pressure of the system; and, last, the IBSD system was moved to a newly constructed, particle-controlled, class 1000 clean room facility. Significant improvement of magnetic and magneto resistive properties of the deposited multilayers was observed following these changes, as will be shown below.

Initially, Ar was used as the sputtering gas in the ion sputter deposition experiments. Figure 13.1 shows an example of a magnetic hysteresis curve (magnetic moment vs. external magnetic field applied in the plane of the sample) obtained from a Si/Cr(50Å)/[Fe(20Å)/Cr(12 Å)]x30/Cr(38Å) multilayer. As can be seen, the remanent magnetic moment in the zero field is approximately zero. This indicates that the magnetic layers in the multilayer structure are almost perfectly antiferromagnetically aligned. The presence of the antiferromagnetic coupling is consistent also with the large magnetic fields, on the order of several thousands of Oe, required to saturate the magnetic moment. Knowing the saturation field $H_s$, one can calculate the exchange coupling constant $J$, which is a parameter characterizing the strength of the antiferromagnetic alignment. The constant $J$ can be calculated using the equation $J = -\frac{H_s M_s t}{4} = -\frac{H_s I}{4A}$, where $M_s$ is the saturation magnetization, $t$ is the thickness of the ferromagnetic layer, $I$ is the magnetic moment of the sample and $A$ is the area of the sample. For the sample of Figure 1, $J$ was equal to -0.4 erg/cm$^3$, comparable to values reported in the literature for the Fe/Cr multilayer system.

An example of magnetoresistance curves obtained for Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38 Å) multilayers deposited using Ar ion beams is shown in Figure 13.2.
The GMR ratio, $MR$, can be calculated from the magnetoresistance curve using the equation

$$MR = \frac{\Delta R}{R},$$

where $\Delta R$ is the difference between the peak in resistance in the zero magnetic field and the resistance in the magnetic field larger than the saturation field $H_s$, and $R$ is the absolute value of the resistance in the large magnetic field. The GMR ratio calculated for the sample of Figure 13.2 is 11%.

Figure 13.3 shows a cross-section, high resolution TEM micrograph of the multilayer of Figure 13.2. The sample for the TEM analysis has been prepared using the focused ion beam (FIB) technique described in detail in a previous report (#2). In order to enhance contrast between individual layers in the multilayer structure, the image has been intentionally defocused. This technique of the contrast enhancement has been mastered in the framework of the MURI program, and was used for analysis of not only MCNC samples, but also metallic multilayer films prepared at the University of Florida, as described in previous reports. The TEM micrograph shown in Figure 13.3 reveals a stack of Fe layers interwoven between Cr layers, as expected. The interfaces between layers are planar and smooth, and their quality is consistent across the whole stack. The high-resolution lattice structure is often coherent across the multilayer, with coherent regions crossing individual layer boundaries. The highly textured structure of the films was also indicated by dark-field TEM and selected area diffraction (SAD) images, as well as by X-ray diffraction spectra.

*Effects of varying the energy of the Ar primary ion beam*

* A priori, the energy of the primary ion beam may influence microstructure and/or chemical composition of the deposited multilayer. These properties in turn affect the GMR ratio. Specifically, the energy of the primary ion beam determines the energy distribution of the sputtered atoms, as well as the energy distribution of neutrals backscattered from the surface...
of the target. Since the working pressure during the IBSD deposition is on the order of 1\times10^{-4} \text{Torr}, sputtered atoms and backscattered neutrals undergo few collisions with the background gas, and, therefore, arrive at the substrate with energies comparable to those they have leaving the target.

Figures 13.4 (a) and (b) show calculated energy distributions for atoms sputtered and backscattered from a Cr target by an Ar ion beam with energies ranging from 300 eV to 900 eV. The calculations were performed using the SRIM (Stopping and Range of Ions in Matter) software based on the Monte Carlo method.

As can be seen from Figure 13.4a, when the energy of the primary ion beam decreases, the plot of the energy distribution shifts to slightly lower energy values. The same is true for the energy distribution of backscattered neutrals shown in Figure 13.4b. In contrast to the sputtered atoms, whose energies lie for the most part below 30-40 eV, backscattered neutrals retain a large portion of the original beam energy with many possessing energies in excess of 150 eV. Energies of sputtered atoms and backscattered neutrals are known to be a determinant in the film growth. With respect to metallic multilayers, as the energy of sputtered species increases, one can expect more intermixing at interfaces, as well as enhanced creation of non-spin-dependent scattering centers. It has been postulated in the literature that the GMR ratio is very sensitive to both of these phenomena.

Experimental data for the GMR ratio for Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38Å) multilayers, deposited for primary ion beam energies of 300, 500, 700 and 900 eV, are shown in Figure 13.5. In all depositions, the ion beam current was equal to 26 mA. In Figure 13.5 resistivity values are plotted as well, again as a function of the primary ion beam energy. It can be seen from Figure 13.5 that as the energy of the primary beam is reduced from 900 eV,
which was the starting point for the series, to 700 eV, the MR ratio increases, while the resistivity stays constant. Further decrease of the ion beam energy results in a decrease of the MR ratio. However, at the same time the resistivity increases significantly. AES analyses revealed that the 500 and 300 eV samples contained a few atomic % of aluminum. The appearance of the impurity is believed to be due to increased spread of the ion beam for the lower beam energies. Due to the increased spread, the beam causes sputtering of atoms from the Al target holder fixture. This spread of the ion beam can be compensated to some extent by adjustment of the voltage applied to the accelerator grid of the ion gun; however, only partial compensation was possible with the ion current chosen for this series. At the next stage of experiments with the Ar working gas, we will use lower beam currents, for which full control of the beam convergence can be more readily achieved.

The presence of the aluminum impurity is a likely culprit for the decreased MR ratio of the Fe/Cr multilayers deposited with the primary ion beam energies of 500 and 300 eV, especially considering the fact that segregation of impurities towards interfaces is often observed in films grown by physical vapor deposition methods. Gurney et al.\textsuperscript{1} reported on effects of third elements deposited at interfaces of RF sputtered Fe/Cr multilayers. When Al was the third element, the MR ratio decreased by a factor of 2 when one monolayer of Al was deposited, and by a factor of 5 when two monolayers of Al were deposited at the Fe/Cr interfaces. The effect is explained by invoking a spin-dependent impurity scattering model, which depicts the multilayer as a distribution of scattering centers whose scattering properties depend on the impurity element and local magnetization direction of the layers into which the centers are embedded.


**Effects of Annealing on Magnetoresistive Properties**

The presented results show that the GMR depends sensitively on deposition conditions. This dependence comes about primarily because the deposition conditions determine the energy distribution of the sputtered atoms, as well as the bombardment of the film by energetic particles. These in turn affect interface roughness and/or formation of non-spin-dependent scattering centers, which are major determinants of the GMR behavior. Interface roughness can also be affected by post deposition treatments such as ion beam irradiation or temperature annealing.

T. Lucinski et al.\(^2\) reported an improvement of GMR ratios in dc-magnetron sputtered multilayers following certain thermal annealing procedures. The effect was attributed to sharpening of the interfaces concomitant with the removal of structural defects such as vacancies and dislocations. To study the effects of annealing on the properties of IBSD Fe/Cr multilayers, the films were vacuum annealed at \(10^{-6}\) Torr for different time-temperature cycles, and the GMR ratios were compared with the values for unannealed samples obtained from the same batch. These annealing experiments were performed at the University of Florida in the group of Dr. Arthur Hebard. For all anneals at 280°C or lower, the GMR ratio either improved or was unaffected; it did not decrease. The largest improvement of 10% occurred consistently for samples sputtered using the primary ion beam energy of 900 eV. One-hour anneals at 280°C gave the same result as 64-hour anneals at 200°C. No improvement was noted for samples obtained with 700eV and lower primary ion energies. If the anneal temperature is too high, then diffusion across the interface decreases the magnetic

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coupling across the interface and decreases the GMR ratio. For example, a 350°C anneal for 2 hours of a 900 eV sample resulted in a 34% decrease in the GMR ratio.

The annealing experiments described above will be extended to samples obtained using Xe primary ion beams (see section II3). Any differences in the post-annealing GMR behavior between samples deposited using Xe and Ar ions might provide insight into relationships between crystallographic defects and the GMR ratio.

In the effort to further optimize the GMR behavior, it is also possible to alloy the Fe layers with impurities to obtain significantly improved performance. For example, Fe$_{0.95}$Cr$_{0.05}$/Cr multilayer films have been reported to have almost a factor of two higher GMR ratio for 10Å-thick Cr layers compared to similar samples prepared without the Cr alloying\(^3\). Samples with high GMR ratios will allow us to critically investigate claims\(^4\) that there is a quantum phase transition from a ferromagnetic to an antiferromagnetic state at low temperatures in layered GMR structures.

### II.3. Fe/Cr Multilayers Deposited with Xenon Ion Beams

Figures 13.6 (a) and (b) compare calculated energy distributions of sputtered Cr atoms (a) and backscattered neutrals (b) for 900 eV Ar and Xe primary ions. The change from Ar to Xe does not affect the energy distribution of the sputtered atoms significantly, as can be seen from Figure 13.6a. On the other hand, the change in the number and energies of backscattered neutrals is dramatic, as can be seen in Figure 13.6b. For a given energy, the number of backscattered neutrals in the case of Xe is significantly smaller than in the case of Ar. In addition, the high energy tail of the distribution extends much further for Ar than for

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Xe. In the Ar case, there is a significant number of backscattered neutrals with energies well in excess of 100 eV.

Figure 13.7 presents a magnetoresistance curve for a Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/ Cr(38Å) multilayer deposited using Xe as the primary ion species; the energy of the ion beam was 900 eV. As can be seen, the GMR ratio calculated from the curve is equal to 25%. As the inset in Figure 13.7 illustrates, the GMR ratio more than doubles in comparison with the multilayer deposited using 900 eV Ar ions. We postulate that the change in the MR ratio is due to the smaller number of energetic backscattered neutrals bombarding the substrate during the deposition in the Xe case. The next stage of experiments with Xe will focus on examining the effects of lowering the beam energy. Based on our experience with the spread of the Ar beam, described in the previous section, we chose a lower ion beam current value of 20 mA for the Xe series. Depositions using the primary ion beam energies below 900 eV and characterization of the deposited films are in progress.

III. Plans For the Next Reporting Period

- Continue development of IBSD for formation of GMR multilayers and spin valve structures. Complete investigations of the effect of the primary ion beam energy on magnetoresistive properties of Fe/Cr multilayers. Extend vacuum annealing experiments to samples deposited using Xe primary ions. Using the deposition process conditions chosen as the result of the optimization process for Fe/Cr multilayers, conduct deposition of Co/Cu and NiFe/Cu multilayers and spin valves. A second ion beam gun will be
incorporated to facilitate the substrate precleaning and modification of the film microstructure through an ion-assisted deposition.

- Continue to support University of Florida and other participating institutions by providing wafers with high resolution liftoff patterns for patterning of magnetic multilayers, performing TEM analyses of deposited materials, designing masks/reticles for use in photolithographic processes and providing device fabrication services. Currently, a fabrication run is in progress to build silicon/thermal oxide/magnetic metal capacitors for an experiment designed by the University of Florida group.

- Optimize processes for formation of contacts to patterned magnetic multilayers using single and dual level metallization schemes.

![Magnetic Hysteresis Loop](image)

**Figure 13.1.** Magnetic hysteresis loop for a Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38Å) multilayer deposited using Ar ions.
Figure 13.2. The resistance vs. external magnetic field for a Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38Å) multilayer deposited using Ar ions with the primary beam energy of 700 eV. The magnetic field was applied in the plane of the sample. The measurement was performed at a temperature of 10 K.

Figure 13.3. TEM micrograph of a Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38Å) multilayer deposited using 700 eV Ar ions.
**Figure 13.4.** Calculated energy distributions for: a) atoms sputtered from a Cr target by an Ar ion beam with the incident energy varying from 300 to 900 eV and b) Ar atoms (neutrals) backscattered from the target. Results based on 5000 ion SRIM simulations.

**Figure 13.5.** Magnetoresistance $MR$ and resistivity $\rho$ of Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38Å) multilayers.
Figure 13.6. Calculated energy distributions for: a) atoms sputtered from a Cr target by an Ar ion beam with the incident energy varying from 300 to 900 eV and b) Ar atoms (neutrals) backscattered from the target.

Figure 13.7. Magnetoresistance vs. magnetic field for a Si/Cr(50Å)/[Fe(20Å)/Cr(12Å)]x30/Cr(38 Å) multilayer deposited using Xe as the primary ion species; the energy of the ion beam was 900 eV. The magnetic field was applied in the plane of the sample. The measurement was performed at a temperature of 10 K.

(S.A.Syed Asif and R.J. Colton, NRL)

The objective of this project is to measure the quantitative mechanical properties of nanostructured materials, thin films of length scale less than 10 nm. Currently depth sensing nanoindentation techniques are popular for measuring the nano scale mechanical properties of materials. However, for ultra-small volumes of materials below a length scale of 10 nm, measuring the quantitative mechanical properties of materials is extremely difficult even using depth-sensing nanoindentation. There are many reasons: difficulty in characterizing the tip shape, unknown thermal drift, floor noise, and poor surface sensitivity of the indentation instrument. Most of the commercial nanoindentation instruments require a minimum of 1 micro Newton (µN) contact load before applying the actual load. Hence, for compliant materials the indenter will penetrate the specimen tens of nanometers and unknown contact damage may occur.

During the past year we have continued our collaboration with Hysitron Inc. and developed the most sensitive and accurate capacitance load-displacement transducer capable of doing force modulation with a force resolution of less than 10 nN and displacement resolution of 0.1 nm. The stiffness sensitivity of the instrument is less than 0.1 N/m capable of detecting long range surface forces. Using this instrument we have measured the quantitative mechanical properties of thin films of thickness less than 30 nm. For example we studied the mechanical properties of Si which is used as a substrate to deposit nanoscale features. Figure 14.1a shows the variation of modulus as a function of contact depth for 30 nm thick SiO₂ film on Si substrate. At higher contact depths (>15 nm), the measured
modulus is 130-140 GPa. The measured modulus compares very well with the modulus of Si (134 GPa) reported in the literature. At shallow contact depths (<15 nm), the modulus decreases and approaches 70-80 GPa for depths about 1-2 nm. The modulus of fused quartz (SiO₂) is ~70 GPa. This clearly indicates that at depth ~1-2 nm the measured modulus is that of the oxide layer (SiO₂) and, as the depth of indentation increases, substrate influence appears since the oxide layer is more compliant than the Si substrate.

Figure 14.1b shows the variation of hardness as a function of contact depth. The measured hardness has the same trend as the modulus. At shallow contact depth (1-2 nm) the hardness is ~5 GPa and it increases to 10-11 GPa at a contact depth of 12-15 nm and remains constant thereafter. As mentioned before, the hardness of Si is ~11 GPa which is almost equal to the pressure required for phase transformation. The hardness of the oxide layer is ~5 GPa (for a contact depth of 1-2 nm). Earlier studies using Atomic Force Microscopy (AFM) technique suggested that the oxide layer on Si is much stiffer and harder than Si. At that time AFM was the only technique capable of measuring mechanical properties of materials less than 10 nm scale. However the AFM technique is only qualitative and in the present form it is not suitable for measuring quantitative mechanical properties.
Another example is the hardness of a nanoscale feature of Ni on Si substrate as shown in Figure 14.2. At depths less than 5 nm the measured hardness is ~ 2 GPa which is the hardness of bulk Ni. The hardness increases as a function of depth and reaches the hardness of Si (11 Gpa) above 30 nm depth. When we first started measuring the mechanical property of these features last year, using the depth sensing technique alone we could not detect the surface and measure the mechanical properties reliably below 50 nm length scale. With our force modulation and phase detection technique we not only measure the traditional hardness of these material below 10 nm scale as shown in Figure 14.2, we could now study the pre-contact mechanics quantitatively.

Figure 14.3 shows the force and interaction stiffness curves during approach and retraction for Si surface with the native oxide layer under ambient conditions (54% RH). The force curve shown here is similar to the force curve measurement in AFM. The interaction stiffness is a convolution of force gradient and contact stiffness between the tip and surface. In general it can be divided into three regimes; pre-contact, apparent- or intermittent-contact, and elastic or elasto-plastic contact regimes as shown in Figure 14.3. The attractive interaction is negative (A-C, A’-C’) and the repulsive interaction is positive (C-D, C’ and beyond). The tip experienced a maximum attractive force of ~180nN and interaction stiffness of 5 N/m. From the force curve measurement the surface energy of the sample can be calculated using the following equation

\[ F = 4\pi R\gamma \]  

(1)

where \( F \) is the attractive force, \( \gamma \) is the surface energy, and \( R \) (~200 nm) is the radius of curvature of the tip (assuming sphere on flat geometry). The calculated surface energy 71.6 mJ/m is in good agreement with the surface energy of water (72 mJ/m). This is expected as
the experiments are conducted under ambient conditions with a relative humidity of 54%. With this capability at present we are working on a theoretical model which will enable us to measure the elastic properties of even a monolayer.

Although we have developed the experimental technique capable of measuring mechanical properties of nano-structures, it is difficult to understand some of the issues, for example the constrain effect. Our experimental results suggest that the nanoscale deformation of a semi-infinite surface is different from two-dimensional or one-dimensional nano-structures. For semi-infinite surface the volume of the deformed zone is much smaller compared to the volume of the material surrounding it and the deformation is constrained by the surrounding zone. For two-dimensional or one-dimensional nano-structures the volume of the deformed zone is almost the same size as the nano-structure hence there is very less or no constrain for the deformation. To address these issues, in the final phase of our project we are planning to do numerical simulation of these deformations along with experimental work.
Figure 14.1  (a) Modulus as a function of contact depth for 30nm SiO2 on Si substrate, (b) hardness as a function of contact depth.

Figure 14.2  Hardness as a function of depth for 50 nm Ni nanostructure on Si substrate.
**Figure 14.3.** Force (♦) and interaction stiffness (+) curves during approach (←) and retraction (→).
15. **Length Scales of Magnetism**

*(F. Hellman, UCSD)*

We have been working on understanding the length scale and magnitude of the magnetism induced in a non-magnetic or nearly magnetic material by proximity to a magnetic material. This is an effect that is well understood in superconducting materials and has led there to practical devices. In magnetism, the effect is less well understood and is generally believed to be extremely local. However, it is clear that in materials which are nearly magnetic, such as Pd or Pt, this length scale will be much longer. As little as 1% Co in Pt leads to a ferromagnetic Curie temperature of over 5K, indicative of the ability of Co to induce magnetism in Pt on a relatively long length. It is also well known that spin diffusion lengths in clean materials (e.g. Cu) can be tremendously long (microns).

We are working with bilayers of materials with different Curie temperatures and measuring the effect of each material on the magnetization in the other. One powerful technique for doing this is to use polarized neutron reflectometry to measure the magnetization profile as a function of depth. Using this method on Co-Pt bilayers of different compositions, we showed that there is an induced moment in the overlayer at least 8K above the overlayer’s $T_c$, indicative of a ferromagnetic proximity effect. Because of the different magnetic and structural scattering factors for Pt and Pd, bilayers of Co-Pt with Co-Pd were expected to lead to better neutron reflectometry. We have therefore prepared epitaxial single crystal bilayers of Co-Pt and Co-Pd alloys in various combinations of concentrations (hence of various combinations of $T_c$) in our UHV evaporation system. In situ RHEED and ex situ X-ray analysis have been done to characterize the structure and chemistry of these films. We initially planned these experiments for LANSCE, but because
of neutron beam delivery problems at LANSCE, graduate student Brian Maranville and collaborator Mike Fitzsimmons did an extended set of neutron reflectometry measurements at NIST. The data proved noisier than anticipated, so we were not able to determine a length scale, but did again see the effect of the underlayer on the overlayer.

These Co-Pt and Co-Pd alloys develop large growth induced perpendicular magnetic anisotropy, which greatly complicates this particular measurement, although it is a useful property under other circumstances. We therefore worked on finding a growth temperature and composition which would allow epitaxial growth of bilayers but not create perpendicular anisotropy or allow significant interdiffusion of the bilayers. We also tried adding trace amounts of Si during growth, which successfully suppressed the magnetic anisotropy, but unfortunately also eliminated the epitaxial growth. We also investigated the properties of Ni-Pt alloys, as these too should show greater contrast in the neutron reflectometry measurements. These alloys also have growth-induced magnetic anisotropy, but less so than Co-Pt alloys, and hence are easier to work with.

In addition to continuing the analysis of the bilayer samples, we plan to prepare multilayers of these modulated composition alloys. With these larger volume samples, we can measure specific heat and magnetization $M(H,T)$, and thereby study the magnetic and thermodynamic properties induced in each material by the other material.
16. Magnetism Of Nanometer-Scale Iron Particles Arrays

(S. von Molnár, FSU)

The magnetization behavior in arrays of small ferromagnetic iron particles has been investigated. Arrays were fabricated by a combination of chemical vapor deposition and scanning tunneling microscopy. This method allows a variety of particle arrays to be grown differing in particle height, diameter or arrangement. Moreover, the arrays can be grown directly onto different materials such as Au or permalloy. Magnetic measurements were conducted by Hall magnetometry up to 100 K and compared to switching field measurements by means of magnetic force microscopy at room temperature. The magnetization reversal mechanisms were studied from magnetization curves measured for an arbitrary angle, theta, of the applied field with respect to the long axis of the particles. By analyzing the reversible rotation, the particles' magnetic core diameter and the shape anisotropy could be determined. A phenomenological model based on thermally activated magnetization reversal was introduced and compared to experimental switching field dependencies on temperature as well as on theta. Thermal effects may govern the magnetization reversal in particles of 10 nm diameter at all temperatures. Particles of 9 nm mean diameter are expected to show a transition to superparamagnetic behavior (with blocking temperature $T(B)$ just below ambient temperature. For 14 nm-particles and temperatures below 30 K, curling (for theta up to 30°) and homogeneous reversal modes appear to dominate.
17. **Theory of GMR**

*(S. Hershfield, UF)*

The year we have extended the work we have done on realistic models of transport in magnetic multilayers. We continue to focus on calculations of the CPP-GMR and on the spin-polarization of the density of states in ferromagnetic alloys.

17.1 **CPP GMR with FeCr as a test case**

We have during the course of this grant developed fully quantum mechanical calculations for the CPP (and CIP) GMR using realistic electronic structure and different kinds of scattering - both surface and bulk. Last year we demonstrated the usefulness of this approach for dealing with large systems, which can be compared directly to experiment. To test the theory, one must know from microscopic probes details about the disorder, e.g., the amount of interdiffusion at the interfaces, variation in layer thickness, etc.

Fortunately, another member of the MURI, Prof. Schuller at UCSD, has undertaken during the last year a series of experiments which characterize the disorder in different FeCr superlattices and at the same time measure the CPP-GMR. Using our approach to calculating the CPP-GMR, we can get values for the GMR and resistivities which agree with those seen in his experiments. We are now working to understand the trends seen in the experimental data with our model.

There is another experimental study on the CPP-GMR in FeCr by Gijs et. al. in the Netherlands (PRL 70, 3343 (1993)). Both our calculations and Schuller's data have larger
resistivities than this data. While this was puzzling for some time, if one assumes that there are alternate current paths in the other experiment to cause the resistivity to be smaller, then one can account for both the smaller resistivity and the size of the GMR which is seen.

This work is done with Jian Chen, formerly a post-doc and now working at Seagate, and with Tat-Sang Choy, a graduate student.

### 17.2 Spin-polarization in the Density of States

The study of the spin polarization of electrons at or near the Fermi level is an active area of research. Experiments are being carried out both by tunneling and by Andreev reflection. There are also a number of theoretical studies of the spin polarization in ferromagnetic alloys. For example, since the 1970's it has been known that microscopic calculations of the spin polarization based on the total density of states lead to the wrong magnitude of the polarization and even in some cases to the wrong sign of the polarization. In the original tunneling experiments of Tedrow and Meservey the spin polarization in the tunneling density of states was correlated with the magnetization of the alloys. More recent Andreev reflection experiments do not see this correlation. Certainly, if the alloy is not ferromagnetic, there should not be any spin polarization in the density of states, but it was not clear if the correlation is any deeper than this.

Starting last year we have undertaken to study this possible correlation in more detail theoretically. Tat-Sang Choy, a graduate student, has performed a series of calculations of both the spin polarization of the s-electrons and the magnetic moment using a tight binding
model in the coherent potential approximation (CPA). For Ni-based alloys we do indeed find
that the spin polarization of the s-electrons and the magnetic moment are correlated and we
do get trends similar to the original experiments of Tedrow and Meservey. However, we also
find that this correlation is not universal. In other words, the correlation depends on the s-
density of states increasing near the Fermi energy. We have examined within our model the
surface density of states and compared it to the bulk density of states. This still leaves open
the question of whether the tunneling experiments and Andreev experiments are measuring
different quantities or whether there is some other difference in the experiments.
Publications


“Simulation of the Interband s-d and Intraband s-s Electron-phonon Contributions to the Temperature Dependence of the Electrical Resistivity in Fe/Cr Multilayers,” B. Almeida, V.


“Magnetoresistance Behavior In $La_{0.7}Ca_xMnO_3$ (X=0, 0.2, And 0.3) Thin Films”, S.V. Pietambaram, D. Kumar, R. K. Singh, Phys. Rev. B. 58, 8182 (1998).


“Growth-Induced Magnetic Anisotropy And Clustering In Ni-Pt Alloys,” A.L. Shapiro, B. B. Maranville, and F. Hellman, Paper in final preparation.


Technical Presentations


“Selective Dry Etching of the GaN/InN/AlN, GaAs/AlGaAs and GaAs/InGaP,” D. Hays, C. Abernathy, W. Hobson, S. Pearton, J. Han, R.J. Shul, H. Cho, K. Kung, F. Ren and Y. Hahn, MRS Spring Meeting, San Francisco, April 1999.


“Magnetoresistance in Rare-earth Chalcogenides-Relationship to Other Rare-earth Compounds,” S. Von Molnar, APS March Meeting, Atlanta, March 1999.

“\( \frac{1}{f} \) Noise in Colossal MR Materials,” A. Anone, B. Racquet, P. Xiong, Z. Fisk and S. Von Molnar, APS March Meeting, Atlanta, March 1999.


“Magnetic Order Of Co_{0.1}Pt_{0.9} In Proximity Of CoPt3,” A. L. Shapiro, oral presentation at MRS Conference, Spring 1998.


Book Chapters

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- W. Teizer   Post Doctoral Fellow at UCSD
- D. Kumar    Research Scientist at UF
- Bernard Revaz Visiting Scholar at UCSD

Graduate Students

- K.B. Jung with Dr. Pearton (now at IBM)
- X. Cao with Dr. Pearton
- K.P. Lee with Dr. Pearton
- J. Mileham with Dr. Pearton (now faculty at U. Puerto Rico)
- H. Hudspeth with Dr. Sharifi
- J. Marburger with Dr. Sharifi
- T.S. Choy with Dr. Hershfield
- J. Lewis with Dr. Holloway
- J. Thomas with Dr. Holloway
- S. Pietambaram with Dr. Sharifi
- G.T. Dang with Dr. Ren
- T. O’Brien with Dr. Holloway
- E. Price with Dr. Hershfield
- A. Shapiro with Dr. Hershfield
- A. Hoffmann with Dr. Schuller
- S.V. Pietambaram with Dr. Singh
- B. Maranville with Dr. Hellman
- A. Shapiro with Dr. Hellman
- Tat-Sang Choy with Dr. Hershfield
Undergraduate Students

S. Getty with Dr. Sharifi
T. Plew with Dr. Pearton
T. Kirk with Dr. Dynes
# Degrees Awarded

<table>
<thead>
<tr>
<th>Name</th>
<th>Degree</th>
<th>Institution</th>
<th>Year</th>
<th>Title</th>
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<tr>
<td>Yun Daniel Park</td>
<td>Ph.D.</td>
<td>University of Florida</td>
<td>1998</td>
<td>“Fabrication and Characterization of Anisotropic MR and GMR Structures at Reduced Dimensions”</td>
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<tr>
<td>D.C. Hays</td>
<td>MS</td>
<td>University of Florida</td>
<td>1999</td>
<td>“Selective Etching of Compound Semiconductors”</td>
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<td>D.S. Bitting</td>
<td>MS</td>
<td>University of Florida</td>
<td>1998</td>
<td>“Aspect Ratio Dependent Etching of SiO$_2$ in HDP Systems for Submicron Applications”</td>
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<tr>
<td>S.T. Molloy</td>
<td>MS</td>
<td>University of Florida</td>
<td>1998</td>
<td>“The Oxidation of TiN in O$_2$ Plasma Photoresist Stripping Processes”</td>
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<td>T.M. Ake</td>
<td>MS</td>
<td>University of Florida</td>
<td>1998</td>
<td>“Ohmic Contacts”</td>
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<td>K. Majumdar</td>
<td>Ph.D.</td>
<td>University of Florida</td>
<td>1999</td>
<td>“Study of Transport Properties in Magnetic Nanostructures”</td>
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<td>A. Hoffmann</td>
<td>Ph.D.</td>
<td>University of California – San Diego</td>
<td>1999</td>
<td>“Fundamental Studies of Magnetism”</td>
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<tr>
<td>A.S. Katz</td>
<td>Ph.D.</td>
<td>University of California – San Diego</td>
<td>1999</td>
<td>&quot;Fabrication, Characterization and Analysis of Nanofabricated Ion Damage High Temperature Josephson Junctions&quot;</td>
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