Final Report: Stability and Novel Properties of Magnetic Materials and Ferromagnet / Insulator Interfaces

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Prof. Chang was supported by various incarnations of the Department of Energy, Basic Energy Sciences, Electron and Scanned Probe Microscopy program from 1999. The direction and nature of his research have evolved substantially over that time. From 1999 to 2002, his group studied diffusion of intermetallics for structural applications at high temperatures such as the prototype triple-defect B2 NiAl, then later tetragonal L1₀ intermetallics. From 2002 to 2005, the project evolved to study antiferromagnetic (AFM) L1₀ materials such as NiMn and PtMn. Sputtered films of these intermetallics have a metastable fcc structure and are not ferromagnetic. He studied the phase transformation of the paramagnetic to antiferromagnetic phase transformation of Pt-Mn and Ni-Mn thin films. That research was Chang's introduction to magnetic materials and the materials problems associated with magnetic data storage, since AFM materials play a key role in giant magnetoresistance (GMR) and magnetic tunnel junction (MTJ) sensors used in magnetic hard disk drives.

From 2005 to 2008, Chang's research shifted to the spin dependent tunneling and interface stability problems inherent to magnetic tunnel junction (MTJ) structures. An MTJ consists of two ferromagnetic (FM) electrodes, one of which has its magnetization pinned to an adjacent AFM layer by exchange bias, separated by an insulating tunnel barrier layer such as AlO_x. PtMn/CoFe/AlO_x/CoFe is a prototype structure, but the synthesis of structures in which fundamental material and interface properties can be meaningfully measured is extremely challenging, since it requires controlling a variety of extrinsic characteristics such as surface and interface roughness and interdiffusion. Chang's group was the first to experimentally isolate and demonstrate the theoretically predicted effect on the junction of the crystal structure of the FM electrode. They isolated the effect of crystal structure from the effect of composition by using strain energy from lattice mismatch with different buffer layers to induce a Co₈₇Fe₁₃ electrode to be either fcc or bcc. They found a significant increase in the TMR for a bcc-Co₈₇Fe₁₃ electrode compared to a fcc-Co₈₇Fe₁₃ electrode, which indicates higher *s*-electron spin polarization for the bcc structure. The higher polarization was confirmed for bulk Co and Co_{87.5}Fe_{12.5} by *ab initio* calculations. These results also showed experimentally that the strain of the FM electrode could change the TMR of a MTJ. By carefully controlling the FM crystal structure, post-annealing effects, and interface roughness and strain states, Chang and his group developed novel approaches to synthesize these structures and obtained the highest TMR at room temperature for AlO_x-based junctions reported in the literature.

Co-PI Paul Voyles joined the project in 2008 and assumed management of the project on Prof. Chang's death in 2011. Prof. Chang was an outstanding mentor, colleague, and friend. This report focuses on the accomplishments of the final two years of the project, which are dedicated to his memory.

High-quality Fe₃O₄ thin films on TiN buffered Si substrates

Fe₃O₄ with ~100% spin polarization (SP) at room temperature (RT) and high Curie temperature of ~850K is a quite promising magnetic material for spintronic devices. Fabricating smooth, low defect density and single phase Fe₃O₄ is essential for achieving high performance in devices like MTJs. We first fabricated Fe₃O₄ thin film on TiN buffered Si (001) substrate by reactive sputtering,¹ however, as shown in **Figure 1** (a), grain boundaries in the film cause large surface

roughness, as indicated by an orange arrow, which suggests that Fe_3O_4 grown by reactive sputtering is not suitable for spintronic devices. Figure 1 (b) shows the magnetization loops for the Fe_3O_4 thin films grown at different substrate temperature. They show that high temperature growth improves the saturation magnetization of the Fe_3O_4 thin films. However, even the magnetization loop of Fe_3O_4 grown at 400 °C shows a hard saturation magnetization even at high applied magnetic field, which suggests that the Fe_3O_4 thin films grown by reactive sputtering have a high density of antiferromagnetically coupled anti-phase boundaries (APBs).²

In order to fabricate Fe_3O_4 thin film with smoother surface and less APBs, we selectively oxidize Fe thin films using a CO_2/CO gas mixture, which allows Fe_3O_4 to form in thermodynamic equilibrium.^{1,3} We have obtained a much smoother Fe_3O_4 thin film with rms roughness 0.34 ± 0.03 nm shown in Figure 1 (b), suitable for spintronics.⁴ We observed a second phase formed at the interface of Fe and TiN after oxidation at 400 °C, but it can be avoided using lower growth oxidation such as 160 °C. The APB structure of a Fe_3O_4 thin film grown at 160 °C with a thickness 19 nm is shown in Figure . The antiphase domain size of the Fe_3O_4 thin film grown at 160 °C is 50~100 nm, which is more than twice the length and four times the area of previous antiphase domains in Fe_3O_4 thin films with similar thickness grown on Al_2O_3 substrate.⁵ The size of antiphase domains in Fe_3O_4 generally increases with film thickness, but the domain size for our Fe_3O_4 thin film is comparable to or even larger than previously reported for 50 nm thick Fe_3O_4 thin films on $\alpha\text{-Al}_2\text{O}_3$ (0001) by MBE⁵ and MgO substrates.⁶ The magnetization loop of this structure (not shown) is dominated by residual Fe below the Fe_3O_4 . We also found at 160 °C, the Fe_3O_4 thickness follows a $1/4$ power law in time.

In conclusion, compared to reactive sputtering, selective oxidation can yield a Fe_3O_4 thin film with low-defect density, smoother surface, which makes this method suitable for nanoscale spintronic applications on Si.

Figure 1 TEM image on Fe_3O_4 thin film grown by reactive sputtering. (b) The magnetization loop of the Fe_3O_4 thin films grown by sputtering at RT, 300 °C and 400 °C substrate temperature. (c) HRSTEM image of $\text{Fe}_3\text{O}_4/\text{Fe}$ bilayer synthesized by selective oxidation. (d) Dark field TEM image using the 220 reflection for the [001] orientated Fe_3O_4 thin film oxidized at 160 °C with a thickness of 19.34 nm.

High-quality Fe_4N and $(\text{Co}_x\text{Fe}_{1-x})_4\text{N}$ thin films on TiN buffered Si substrate

Fe_4N is a promising material for spintronic devices with nearly -100% SP at Fermi level at RT.⁷ We fabricated Fe_4N thin films by reactive sputtering⁸ and explored several growth parameters including substrate temperatures and N_2 concentrations. Annealing the Fe_4N thin film under 30 % N_2 gas environment can prevent the Fe_4N from decomposing as it will in air or vacuum at that temperature. Epitaxial Fe_4N thin films prepared at 300 °C and 30% N_2 are shown in the **Figure 2(a)**, which shows a good epitaxial relationship. In Figure 2 (b) EELS data shows that the N/Fe

atomic ratio is 0.2 ± 0.027 , which means the resulting Fe_4N film is nearly stoichiometric. Magnetic property were also investigated. We found that after post annealing the sample, the magnetization easy axis followed the Fe easy axis [110] which is also consistent with the XRD data.

Fe_4N is metastable and easily decomposes by N desorption during interfacial oxidation and Fe_3O_4 formation as shown in Figure 2 (c). In Figure 2 (c), there is oxide layer on top of Fe_4N thin film after leaving the uncapped Fe_4N thin film in air. EELS spectrum of the oxidation layer is consistent with our measurement on a Fe_3O_4 standard. The phase transformation from Fe_4N to Fe_3O_4 at RT is thermodynamically favorable, since the standard Gibbs formation energy of Fe_4N and Fe_3O_4 are +3.8 kJ/mol and -1015.4 kJ/mol, respectively. At the Fe_4N / Fe_3O_4 interface, an intermediate layer also shows up in Figure 2(c). The intermediate layer has a bigger lattice constant than the Fe_4N thin film. EELS result in Figure 2 (d) also shows N K, O K and Fe L edges on the intermediate layer. EELS quantification shows that the composition of the intermediate layer is close to $\epsilon\text{-Fe}_2\text{N}$, which is consistent with previous work.^{9,10,11} In addition, both Fe_3O_4 and Fe_4N have the cubic crystal structure. Since the lattice parameter of Fe_4N (0.3795 nm) is about half of that of Fe_3O_4 (0.8396 nm), eight Fe_4N unit cells can convert into one Fe_3O_4 unit cell with ~10% lattice mismatch, which makes the formation of Fe_3O_4 on Fe_4N lattice favorable.

Co_4N is also a ferromagnetic material with the same fcc structure as Fe_4N .^{12,13} Similar to Fe_4N , Co_4N has the minority spin electron dominant conduction current, which was recently predicted to be nearly half metallic.^{12,13} However, growth by reactive sputtering with low Co flux led to only Fe_4N peaks in the XRD. **Figure 3** (a) shows the $(\text{Co}_x\text{Fe}_{1-x})_4\text{N}$ thin film grown at low flux on TiN buffered Si substrate. Without capping layer on top of the thin film, an oxidation layer formed. In the HRSTEM image shown in Figure 3 (b), the surface oxidation layer has a similar structure as shown in Figure 2 (c). The EEL spectrum on the surface oxidation layer also has a pre peak in O K edge but no Co L edge shows up in Figure 3 (b), which means the surface oxidation is

Figure 3 (a) HRSTEM image of all three layers from bottom to top is Si, TiN and Fe_4N , separately; (b) EELS spectrum on Fe_4N layer. (c) surface oxidation of Fe_4N . Three layers in the (c) are identified as Fe_3O_4 , $\text{Fe}_2\text{N}_{1-x}$ and Fe_4N . (d) The spectrum taken on the Fe_3O_4 layer shows O K and Fe L edge. (e) The spectrum taken on the intermediate layer shows N K, O K and Fe L edges.

Figure 2 (a) A HRSTEM image of the interfaces between surface oxide and the $(\text{CoFe})_4\text{N}$ thin film with low Co concentration. (b) and (c) are EEL spectra from surface oxide and the film, respectively. (d) A HRSTEM image of the interfaces between surface oxide and the $(\text{CoFe})_4\text{N}$ thin film with high Co. (e) and (f) are EEL spectra from surface oxidation layer and thin film, respectively.

completely Fe oxide. EEL spectrum in Figure 3 (c) shows that only Fe and N edges are presented, which might be due to the small Co depositing power.

Figure 3 (d) shows the thin films deposited with higher Co flux. The surface still has a thin layer of oxidized layer, but it is smoother than the low-flux film. EEL spectrum on the surface oxidation layer in Figure 3 (e) reveals that the oxidation layer contains Co and Fe with a Fe/Co ratio 0.52 ± 0.12 . EEL spectrum on the thin film in Figure 3 (f) shows almost only Co L edges with Fe/Co ratio 0.12 ± 0.01 and without N K edge. From that result and XRD, we conclude that the film contains fcc Co (002) instead of Co_4N or $(\text{Co}_x\text{Fe}_{1-x})_4\text{N}$.

In conclusion, we fabricated Fe_4N thin films by reactive sputtering, but we failed to fabricate Co_4N thin films due to its poor nitride formability by investigating through a series of $(\text{Co}_x\text{Fe}_{1-x})_4\text{N}$ thin films.

$\text{Fe}_4\text{N}/\text{AlO}_x$ interface in a $\text{Fe}_4\text{N}/\text{AlO}_x/\text{Fe}$ MTJ investigated by HRSTEM and STEM EELS

We integrated Fe_4N electrodes in MTJs with AlO_x as the tunnel barrier and Fe as one of the electrodes. Field cooling was done in air by keeping the as-prepared sample at 250 °C for 2 min and then cooling it to RT under a 1000 Oe magnetic field. **Figure 4(a)** and (b) show that the sign of the tunneling magnetoresistance (TMR) has changed before and after field cooling. Positive TMR (3.3% under 0.02 V bias) is shown for the MTJ before field cooling, which is abnormal for a MTJ with a ferromagnetic electrode having negative spin polarization. However, after field cooling, we have a negative TMR instead (-5.7% under 0.02 V bias).

HRSTEM and STEM EELS were applied to investigate the structures of the MTJs, especially the interface of $\text{Fe}_4\text{N}/\text{AlO}_x$, before and after annealing. In Figure 4(c), we found a reaction layer formed at $\text{Fe}_4\text{N}/\text{AlO}_x$ interface in the MTJ before field cooling (as deposited). The reaction layer has a many defects but also a different crystal structure from the Fe_4N thin film. After annealing, in Figure 4(d), the similar is present, but it has improved crystal quality. The crystal structure of the reaction layer is similar to that of Fe_3O_4 along a [110] zone axis.

Figure 4(e) and (f) show EEL spectra before and after annealing, respectively. Both spectra show the pre-peak feature on the O K edge, which is consistent with the formation of some FeO_x phase.¹⁴ Quantification of the reaction layer EELS as deposited shows that the Fe/O ratio is 1.1 ± 0.1 , close to FeO. EELS quantification on the reaction layer of junction after annealing shows 0.8 ± 0.1 , which is close to Fe_3O_4 . The formation of Fe_3O_4 is consistent with our results on the oxidation behavior of Fe_4N .

In conclusion, we investigated the TMR, bias dependence, and microstructure of $\text{Fe}_4\text{N}/\text{AlO}_x$ based MTJs. HR-STEM characterization finds a reaction layer at the $\text{Fe}_4\text{N}/\text{AlO}_x$ interface which is primarily Fe_3O_4 , with possible FeO or extra oxygen in the as-prepared state. After 250 °C field cooling, the EEL spectra show decreasing Fe/O ratio from

Figure 4 (a) and (b) show the TMR of the $\text{Fe}_4\text{N}/\text{AlO}_x/\text{Fe}$ MTJs before and after field cooling, respectively. (c) and (d) show the HRSTEM images of the interfaces for the MTJs before and after annealing, respectively. (e) and (f) show the EELS on the interface reaction layers before and after annealing, respectively.

Figure 5 STEM EELS results on the inverse TMR after field cooling. (a) O K edge ELNES extracted from the barrier, upper and lower interfaces. (b) Fe L edge core level shift between upper and lower CoFe/AlO_x interfaces (c) simultaneous HAADF image on the area where EEL SI was taken. (d) the intensity map of the pre peak of O K edge

1.1 ± 0.1 to 0.8 ± 0.1 , indicating the diffusion of the extra oxygen towards the AlO_x barrier and improved Fe₃O₄ quality. The as-prepared junctions have normal TMR, which may result from the combination of an imperfect Fe₃O₄ layer containing FeO and extra oxygen at the reaction layer / insulator interface. We attribute the abnormal bias dependence to the formation of FeO_x before and after field cooling.

CoFe/AlO_x interfaces of the inverse TMR MTJ investigated by HRSTEM and STEM EELS

We observed inverse TMR an MTJ with a symmetric structure Si (001) / Ag (buffer) / CoFe / AlO_x / CoFe / IrMn / Ag after it was annealed in air at 200~300 °C for 2 min, then cooled to room temperature under a 1000 Oe magnetic field. STEM EELS spectrum imaging shows that a thin, discontinuous layer of Fe₃O₄ at the interface is the reason for the inverse TMR.¹⁵ Fe L edge core level shifts extracted from STEM EEL spectrum images taken at the interfaces of the inverse TMR junctions show the formation of Fe₃O₄ at the interface of CoFe/AlO_x.

In **Figure 5** (a), the O K edge ELNES extracted from the bottom interface of CoFe/AlO_x shows a pre-peak but none was observed at the lower CoFe/AlO_x interface and the AlO_x barrier. The splitting between pre-peak and main peak agrees with our measurement on a Fe₃O₄ standard. The Fe L edge core level shift shown in Figure 5(b) shows a shift of 0.5 eV to higher energy compared to FeO, consistent with Hofer *et al.*¹⁶ The simultaneously-acquired HAADF image is shown in Figure 5(c) and the intensity map of the pre-peak of O K edge is shown in Figure 5(d), which also indicates the Fe₃O₄ formed only at the bottom CoFe/AlO_x interface. Fe₃O₄ is also found at the top interface. STEM EELS shows no sign of Fe₃O₄ at the interfaces of the MTJs with the TiN buffer and normal TMR, indicating that Fe₃O₄ is the reason for the inverse TMR.

We observed inverse TMR only in Ag-buffered samples after annealing and field cooling. We believe it is due to the high O solubility in Ag. O has a relatively high solubility in Ag (about 2.24 c.c./g at 300 °C),¹⁷ so we speculate that the annealing released the O from the Ag, it diffused to the tunnel barrier, then reacted with Fe in the electrodes to form Fe₃O₄. Although these MTJs are not optimized for the inverse TMR, they represent a particularly simple processing path to achieving inverse TMR, just by annealing. This may point to an easier way to control inverse TMR by manipulating the O in Ag using the annealing time and temperature. Other materials as buffer or capping layers might also be useful as oxygen reservoirs, like Ta, Ti, Zr and Hf, which also have high O solubility.^{18,19}

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