Nanocharacterisation of magnetic structures

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Abstract. Analytical electron microscopy is a powerful tool for investigating the structural and chemical properties of magnetic materials with high spatial resolution. This is illustrated by results from two specific examples. Firstly, we show that while the MnPt layer in CoFe/MnPt exchange biased bilayers transforms from the non-magnetic fcc phase to the magnetic fct phase during annealing, the annealed MnPt layers also exhibit an undesirable increase in grain complexity. Secondly, we use electron energy loss spectroscopy to obtain elemental profiles in spin tunnel junctions being developed for MRAM application. In particular, we use the near edge fine structure present on the O K-edge to separate the signals from the AlOₓ barrier layer and other oxides present in the sample.

1. Introduction
Successful performance of magnetic devices such as spin tunnel junctions or spin valves requires the magnetic layers in the structure to have precisely controlled magnetic coupling between the layers and a well defined response to an applied field. This places high demands on the physical structure of the layers. Important properties include crystallographic structure, composition, grain size, layer thickness and whether or not a texture axis exists. Even more important, however, is the quality of the interfaces between the different layers as roughness, intermixing or diffusion of elements across interfaces can all affect the magnetic and transport properties [1]. Thus, for example, if conformal layer roughness is present in a structure in which a non-magnetic spacer separates two ferromagnetic layers one of which is pinned by an antiferromagnet, the resulting hysteresis loop is offset from the origin. This is a result of magnetostatic (the so-called Neel) coupling between the layers [2]. Its presence is generally undesirable as the fields required to switch the layer with lower coercivity are no longer of equal magnitude for the forward and reverse directions as a consequence of the offset.

The range of imaging and analytical techniques provided by transmission electron microscopy (TEM) make it an excellent tool for investigating the layers and interfaces in magnetic multilayer structures. The first set of results in this paper is from exchange biased layers in which the antiferromagnetic layer is MnPt. The as-deposited MnPt layer is face centered cubic (fcc) and is non-magnetic. However, upon annealing at elevated temperatures the MnPt becomes antiferromagnetic after a structural transition to the ordered face centered tetragonal (fct) phase. A high degree of ordering during the phase transition depends on the right annealing conditions and is a prerequisite for enhanced exchange bias [3,4]. TEM was used to investigate whether observed differences in magnetic properties of various samples could be correlated to either differences in the MnPt grain size or the degree of ordering (i.e. the relative amount of fct phase formed). The second set of results concentrate
on the width/roughness of the barrier layer in spin tunnel junctions which are being developed for MRAM application. There are several challenges to measuring the width of the oxide barrier layer in such samples. Surface oxidation of the TEM specimen can lead to the detection of oxygen in other layers in the structure. The projection problem in TEM can make it difficult to differentiate between diffusion profiles and the effects of interface roughness and/or misorientation of the interfaces in the electron beam. Other effects resulting from probe tails and specimen drift can further confuse the issue. However, probe tail effects can be estimated using a sample with a sharp interface orientated along the beam direction. Effects arising from specimen drift can be investigated by comparison of different datasets combined with knowledge of the direction of any drift during acquisition. In the case of the oxide barrier layer, the use of electron energy loss near edge fine structure (ELNES) offers a potential method of separating the effects of diffusion, surface oxidation and roughness. Since the chemical state of the atom determines the ELNES, it is often possible to separate out the contributions to an edge from atoms in different phases. One would expect to see differences in the ELNES of the O K-edge from the AlO$_x$ layer and the oxidised ferromagnetic layers. Here we explore the use of the ELNES to separate the AlO$_x$ signal from other oxides present in the structure.

2. Experimental

A range of exchange-coupled bottom-pinned MnPt/CoFe bilayers containing a Mn$_{51.5}$Pt$_{48.5}$ layer (of thickness 8.5, 20 or 30 nm) were prepared in an automated Nordiko 2000 magnetron sputter system. The layers were deposited onto Si$_3$N$_4$ membrane windows for plan view investigations. Samples for cross-sectional studies were deposited onto a glass substrate with an Al buffer layer.

The spin tunnel junctions were prepared on Si/SiO$_2$ substrates by ion beam deposition and oxidation using a Nordiko 3000 tool. They had the following nominal structure (layer thicknesses in nm): Ta 9/NiFe 5/MnIr 9/CoFeB 4/Al 0.9+oxidation/ NiFe 7/Ta 3/TaO 2. The film compositions, as determined by a combination of Rutherford back scattering (RBS), elastic recoil detection analysis (ERDA) and particle-induced X-ray emission (PIXE) techniques, were Ni$_{80}$Fe$_{20}$, Co$_{74}$Fe$_{16}$B$_{10}$ and Mn$_{74}$Ir$_{26}$. The barrier was formed by remote plasma oxidation of the 0.9 nm thick Al films. After deposition the structures were annealed for 40 minutes at 280 °C in vacuum, under a magnetic field of 3000 Oe for exchange field setting and to improve the (111) texture [5].

Cross-sectional TEM specimens were prepared by standard grinding, polishing and dimpling methods. Final thinning was achieved by Ar ion milling in a Gatan PIPS (precision ion polishing system). The specimens were examined in an FEI Tecnai F20 TEM/STEM equipped with a field emission gun, a Gatan ENFINA electron spectrometer and an EDAX X-ray spectrometer. EELS (electron energy loss spectroscopy) spectrum imaging was performed using Gatan Digital Micrograph and DigiScan software. Typical operating conditions for the EELS used in this work consisted of a ~0.5 nm diameter probe with 23 pA of current and a semi-convergence angle of 8.8 mrad. In the case of the samples deposited on Si/SiO$_2$, the single crystal Si substrate was used to orientate the sample such that the growth direction was perpendicular to the electron beam direction.

3. Results

3.1.1. CoFe/MnPt bilayers. There was no exchange bias present in the as-deposited bilayers. However, after annealing all of the bilayers exhibited exchange bias [6,7]. The exchange bias was observed to increase with layer thickness up to ~20nm after which there was no further increase. TEM analyses showed that there was no observable residual fcc MnPt phase remaining in the annealed samples and hence the differences in exchange bias could not be attributed to differences in the relative quantities of the two phases. Figure 1 contains bright field TEM images and selected area diffraction patterns from an as-deposited sample and after annealing. The rings in the selected area diffraction pattern from the as-deposited sample index as fcc MnPt, fcc CoFe and hcp Ru. After annealing the MnPt rings index as fct confirming that the fct MnPt phase has formed. If both MnPt phases were present in a sample, the fcc phase could be identified by its (220) reflection which would appear between the (220) and (202) reflections of the fct phase. The bright field images clearly show
differences in the average grain size and complexity. The as-deposited sample has grain sizes of \( \approx 10 \text{nm} \) in-plane. After annealing the grains become more complex in shape, exhibit twinning and have a larger distribution of sizes ranging roughly between about 10 nm and 100 nm in-plane. Increasing complexity with increasing MnPt layer thickness was observed in both plan view and cross-section. The cross-sectional studies showed that while many of the grains in the annealed MnPt layers were columnar there were also regions in the 20nm and 30nm MnPt layers where the grains were not continuous through the layer thickness. Thus the average out-of-plane grain size is less than the MnPt thickness in the 20nm and 30nm MnPt layers. This is in agreement with XRD measurements where saturation in average out-of-plane grain size was observed at \( \approx 18 \text{nm} \). Hence the observed differences in grain size and complexity offer an explanation for the saturation in exchange biasing observed at MnPt layer thicknesses of \( \approx 20 \text{nm} \).

Figure 1. (a) Bright field TEM image and (b) selected area diffraction pattern of as-deposited MnPt bilayer. The rings labelled on the right hand side are from the \textit{fcc} MnPt phase. (c) Bright field TEM image and (d) selected area diffraction pattern of MnPt bilayer after a rapid thermal anneal (set temperature 210°C for 3 mins with a peak temperature of 300°C). The rings labelled on the right hand side are from the \textit{fct} MnPt phase.

3.1.2. \textit{Investigation of barrier width in spin tunnel junctions for MRAM application.} We have previously reported some results on these spin tunnel junctions \cite{8,9}. The TEM investigations showed that the ferromagnetic layers in these samples were all crystalline with similar in-plane grain sizes of \( \approx 10 \text{nm} \), as estimated from the cross-sectional TEM images. The AlO\(_x\) barrier layer in these samples was amorphous. Here we investigate a method of measuring its width from the O K-edge in EELS.

The non-uniform nature of the barrier is seen in the HREM image in figure 2. In the field of view the amorphous AlO\(_x\) layer width appears to vary from \( \approx 0.8 \text{nm} \) to \( \approx 1.6 \text{nm} \). Variations in the observed width of the barrier layer were also observed in HAADF STEM images as shown in figure 3. Here the
oxide barrier layer appears as a thin narrow dark layer as a result of its low mean atomic number. Examination of figure 3 also shows some roughening of the other interfaces present in the structure. An EELS spectrum image covering the energy range of the O K, Mn L, Fe L, Co L and Ni L-edges was collected along the line indicated on figure 3. The spectrum image is shown in figure 4 after removing the background under the O K-edge. In this image the horizontal axis corresponds to energy loss while the vertical axis is the position across the layers with the growth direction running from top to bottom. Bright areas correspond to the EELS edges. Elemental distributions were obtained from the edges in the original spectrum images as follows. The background was removed using the standard procedure of fitting a power law function (of the form $AE^{-r}$) to the background preceding the edge, extrapolating it under the edge and then subtracting. The intensity was integrated in a 50 eV window starting at the edge onset. The resulting elemental distributions obtained for O, Mn, Fe, Co and Ni are shown in figure 5. The oxygen profile shows the presence of some oxygen throughout the sample; this results from surface oxidation of the TEM specimens. The width of the barrier as determined from the FWHM of the peak in the oxygen signal is $\approx 2.3$ nm but, because of the other oxide contributions present, it is difficult to discern the full extent of the barrier.

However, rather than just showing the O profile we can use the ELNES to create phase distributions. The difference in ELNES on the O K-edge is illustrated clearly if we compare the O K-edge from the AlO$_x$ layer, the TaO$_x$ and the surface oxide shape as shown in figure 6. The surface oxide shape was determined by summing the small O K-edges from the MnIr, CoFeB and NiFe layers. The phase profiles were obtained by subtracting the background under the O K-edge and using a multiple linear least squares (MLLS) fitting procedure to model the edge shape in each spectrum as a linear combination of the reference spectra in figure 6 over the energy range 530-560eV. The resulting weights from the fits are shown in figure 7. The measured width of the barrier at this point as determined by the FWHM again measures as $\approx 2.3$ nm. However, it is now much easier to discern the extent of the AlO$_x$ layer which is $\approx 3.6$ nm. This was the maximum width measured by EELS for the barrier in this sample and arises from the growth of the underlying layers. The HAADF STEM image shows that at this position on the specimen, the bottom Ta/NiFe interface is clearly not perpendicular to the growth direction.

![Figure 2. HREM image of a spin tunnel junction showing the non-uniform nature of amorphous AlO$_x$ barrier layer.](image-url)
Figure 3. HAADF STEM image of STJ.

Figure 4. EELS spectrum image collected along the line shown in figure 3. The background has been removed under the O K-edge.

Figure 5. EELS elemental profiles obtained from spectrum image. These are scaled to the same maximum height.

Figure 6. Summed O K-edges from AlO_x, TaO_x and surface oxide. These have been scaled to the same height and offset for clarity.

Figure 7. Weights from MLLS fit to O K-edge using edges in figure 6.
4. Conclusions
TEM investigations of CoFe/MnPt exchange biased bilayer showed that the MnPt layer transformed from the non-magnetic \textit{fcc} phase to the magnetic \textit{fct} phase during annealing. No residual \textit{fcc} MnPt phase was observed after annealing. While the annealed bilayers exhibited exchange biasing, the increase in grain complexity was undesirable. Ideally one would want to obtain exchange biasing while retaining control over the microstructure.

EELS was used to measure the width and extent of an oxide barrier layer in a spin tunnel junction being developed for MRAM application. Here the ELNES on the O K-edge was used to separate the oxygen signal in the \textit{AlO\textsubscript{x}} layer from other oxygen contributions in the specimen. In the presence of other O contributions, this method allows one to discern the extent of the \textit{AlO\textsubscript{x}} layer much more clearly.

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