Characterisation of Magnetic FeRh Epilayers

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Abstract. The lattice structure of roughly equiatomic iron-rhodium epilayers was studied using transmission electron microscopy. Thin films were grown on magnesium oxide substrates using molecular beam epitaxy with thicknesses of 50 nm and capped with a 2-3 nm thick MgO or Al cap. The samples were prepared into cross-sections for characterisation by TEM. Observation of the interfaces FeRh makes with the cap and the substrate are of interest, due to the potential for strain and interfacial diffusion, which will affect the magnetic properties. TEM imaging combined with X-ray photoelectron spectroscopy depth profiling data give an insight into how strain and diffusion at the interface can affect the magnetic transition.

1. Introduction

The magnetic properties of iron-rhodium (FeRh) alloys are extremely unusual, making them an interesting area of research. When in a roughly equiatomic state (i.e. Fe₄₈-Rh₅₂ to Fe₅₆-Rh₄₄), the alloy is in an ordered α′ state and arranged in a CsCl structure[1]. At room temperature, FeRh exhibits antiferromagnetic (AFM) behaviour. It undergoes a first order phase transition to ferromagnetism (FM) at ∼350 K[2] and has a Curie temperature of 675 K[3].

The transition also involves a uniform 1% increase[4] in unit lattice volume when entering the ferromagnetic phase, which is a lattice parameter jump from 2.987 Å to 2.997 Å[1] (a change of 0.03%). Other characteristics of the phase change include an increase in entropy and resistivity when changing to the FM phase as well as a ∼10 K temperature hysteresis[5]. The properties of the phase change can be altered and thus controlled by changing the structure of the FeRh through several techniques, including ion beam irradiation[6] and doping with various elements[7]. One other such method of altering the magnetic transition discussed here is growing FeRh epitaxially onto a substrate with a small (<5%) lattice mismatch. The epitaxial growth causes a compressive or tensile strain on the FeRh lattice (depending on whether the substrate is lattice parameter is larger or smaller than that of FeRh), thereby causing an increase in the transition temperature with a compressed lattice and vice versa.

Due to the magnetic phase change and its ability to be tuned to specific temperatures, FeRh has potential uses for spin valves in magnetic data storage or microelectromechanical systems. The ability to constrain the lattice via a substrate could yield nanoscale switchable magnets if grown on a piezoelectric substrate.

There is an interest in using electron microscopy to fully characterise the FeRh system in a thin film state. Much work has been done on the magnetic properties of the transition but little has been done to relate these properties to the nanostructure of the thin films. In particular,
there is much interest in the regions surrounding the interfaces because of the changes in structure and magnetism.

Experiments with polarised neutron reflectometry\cite{8} revealed, for 50 nm FeRh epilayers grown on MgO and capped with 2 nm of MgO, after cooling through the transition to the AFM phase there were still latent FM moments in the film, as demonstrated in figure 1 by the increase in magnetic scattering length density (SLD). The measurement of SLD arises from measuring the reflectivity as a function of the spin eigenstate of a neutron being parallel or antiparallel to a direction defined by an applied magnetic field. For the magnetic SLD profiles, the value is zero for AFM domains and non-zero for FM domains. The structural SLD changes depending on the density, meaning different elements and isotopes will yield different values. The results show that the difference in magnetic phase is constrained to 6-8 nm from both cap and substrate interfaces. It theorised (by Fan et al)\cite{8} that diffusion at the interfaces and imbalances in the Fe:Rh ratio could influence this metastable phase. Structural scattering length-density information shows there could be a change in composition or density close to the interface, as shown in figure 1.

Transmission electron microscopy is an ideal method to characterise this as it can provide direct structural information as well as combine it with compositional data from energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Structural and magnetic scattering length-density (SLD) depth profiles for FeRh above and below the transition temperature obtained from the CRISP reflectometer at ISIS. The increase in the magnetic SLD at 300 K shows the presence of ferromagnetic domains close to both interfaces. The change in the structural SLD suggests a Fe-deficient (Rh-rich) area towards the cap which could explain the FM region\cite{8}.}
\end{figure}

2. Experimental

The FeRh films were grown via molecular beam epitaxy onto an MgO substrate, codeposited from separate Fe and Rh sources at a rate of 0.3 Å/s. The pressure during growth was $5 \times 10^{-10}$ Torr and the substrate temperature was kept at 300 K. The samples were then annealed at 800°C for an hour then capped in-situ with a 20-30 Å layer of MgO or Al.

For observation in the TEM, the samples were cut into cross-sections. The thin films were cleaved in half and fixed together with epoxy, then encapsulated in a molybdenum wire surrounded by brass tubing. 800 µm discs were cut using a low-rpm saw (Buehler IsoMet) and hand-ground to a thickness of 80 µm. Using a dimple grinder (Gatan 656), the middle of the samples were thinned to 20 µm. The final step utilised a precision ion polishing system (Gatan 691) with an Ar ion source. The sample was thinned with a 5 keV beam until a hole formed in the middle and then smoothed at 2 keV. The typical thickness around this hole should be ~20 nm. The samples were characterised in a FEI Tecnai TF20 at 200 kV.

Cross-sectional samples were also prepared for TEM observation by focused ion beam with a FEI Nova 200 NanoLab FESEM with a Ga ion source. A layer of carbon ~30 nm thick was deposited on the film to prevent the beam damaging the crystalline structure. A layer of platinum was deposited over the area of interest to protect the area during milling. A 30 kV beam at 20 nA excavated on both sides of the area of interest to a depth of 5 µm. The sample
was then thinned further using a beam current of 100 pA. The sample was lifted out in-situ by welding to a micromanipulator and moved to a TEM sample holder.

In order to provide elemental analysis of the cap-film interface, X-ray photoelectron spectroscopy measurements were performed on a VG Escalab 250 with an Ar-source ion beam attachment to allow for depth profiling in plan view through the sample. Measurements were taken at varying intervals in the sample from the surface up to 12 nm.

The results of two samples are discussed in this paper. The first, used for TEM images, is a 50 nm FeRh epilayer grown on an MgO substrate with a 2 nm MgO cap. The second is another 50 nm FeRh epilayer on MgO, doped with a small amount of Pd and a 3 nm Al cap, used for XPS interfacial analysis.

3. Results and Discussion

Initially, it is interesting to compare the focused ion beam and conventional sample preparation methods. There was difficulty preparing samples using FIB as the material would redeposit in structures in front of the sample, blocking the beam until it was ablated. A potential reason for this would be that ion beam irradiation is causing areas to become ferromagnetic. A method by Aikoh et al[6] has shown how Ga ions in a FIB could lower the effective transition temperature of the material, forcing it into a ferromagnetic phase. Once the sample was prepared with FIB, the major difference compared to conventional sample preparation was the thickness. The samples prepared with the FIB were ∼60-90 nm in thickness whereas ones prepared via the conventional method were ∼20 nm thick. The images obtained from conventional TEM cross-

sections demonstrate the high level of coherence (figure 2) at the FeRhMgO substrate interface, which is to be expected considering the epitaxial method of growth. The expected epitaxial relationship is FeRh[100][001]∥MgO[110][001]. For FeRh, the (110) direction is 4.224 Å, while the MgO lattice parameter is 4.21 Å(100), a 0.24% difference. It is evident from the images shown in figure 2 that the lattice matches over the interface although there is little evidence of any dislocations in the structure. Comparing to the interface at the MgO cap in figure 3, there is still a degree of coherence although it is less pronounced. Also, there is a ∼2-3 nm thick contrasted area along the interface in the FeRh film that could suggest that the lattice is being extensively strained or there is a difference in the material composition in this area.

Figure 2. TEM images of the FeRh/MgO substrate interface. The image demonstrates the coherence of this interface, due to the epitaxial nature of the thin film growth. The FeRh film is the darker area towards the top while the MgO area is the lighter area at the bottom.

Figure 3. TEM images of the FeRh/MgO cap interface. The coherence at this interface is far less pronounced than at the substrate interface shown in figure 2. There is a contrast ∼2-3 nm thick that runs along the FeRh side of the interface, suggesting potentially a lattice strain or a change in composition along this region.
Depth profile results from the XPS analysis of a sample with an Al cap, although only focused on the FeRh:Al cap interface, give a good insight into the latent ferromagnetic region as seen by Fan et al. Even past the interface there is still a presence of Al in the FeRh film, as shown in figure 4. The depth of this area is \( \sim 2 \) nm, which is the same as that of the contrasted area found in the TEM sample. This could also, however, be due to redeposition of the Al that was sputtered from the sample during depth profiling. There is also a change in the Fe:Rh ratio within this area, as well as evidence for diffusion of the FeRh through into the Al cap.

**Figure 4.** Depth profile data taken using XPS of an FeRh epilayer with an Al cap. The FeRh/Al interface is shown at 3 nm. It is clear that quantities of Al have diffused across the interface as significant quantities of Al are detected beyond the interface.

### 4. Conclusions

The results of the XPS give backing to the theory that interfacial diffusion, potentially driven by strain on the lattice, is affecting the magnetic transition at the interface. The TEM images of this interface show a high contrast that could be explained by a large amount of strain being applied to the FeRh lattice at the interface or by a change in composition. Further research with TEM cross-sections could give information into how the interfacial diffusion is affecting the lattice structure of the FeRh and, ultimately, how it is driving changes to the phase transition.

Further research into the FeRh system can focus on the lattice structure during the transition. By using a heating system in-situ, the strain on the lattice can be observed in real time to see how the transition nucleates and grows in a constrained thin film sample.

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