Interface chemistry and structure of multiply oxidized barrier spin-tunnel junctions

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Nb/Fe/Al_2O_3/CoFe/Nb spin-tunnel junctions fabricated using a multiple oxidation technique have been characterized using high spatial resolution electron microscopy techniques. Junction magnetoresistance values up to 6.2% at room temperature and 9.2% at 77 K were obtained for junctions fabricated using this technique. Energy dispersive x-ray spectroscopy and electron energy loss spectroscopy were used to study the chemistry and interface structure of the barrier layer; elemental mapping showed the degree of chemical homogeneity across the layers and high spatial resolution electron energy loss spectroscopy revealed changes in the oxidation state and *d*-shell occupancies of Fe and Co across the layers, which need to be considered when modelling the spin-tunneling effect. Pinholes across the barrier were also observed by high resolution electron microscopy. © *2000 American Institute of Physics.* [S0021-8979(00)32408-2]

I. INTRODUCTION

The chemical state and interface morphology of the insulating barrier layer in a spin-tunnel junction are critical in controlling the magnetoresistive characteristics of the junction. Although this realization seems to have led to the trial of a number of different fabrication techniques using a variety of oxidation methods and junction structures, much needed interface structure and chemistry information is still scarce. It has been shown that a range of junction magnetoresistance (JMR) values are obtainable depending on the method used to form the oxide junction barrier. The most successful methods seem to be oxidation in atmosphere for which a JMR of 18% at RT has been reported,[1] and plasma oxidation for which JMR values up to 25% have been reported.[2] More recently a multiple oxidation method, which involves repeated deposition and oxidation of the Al to create the barrier layer, has been used, and JMR values up to 6.2% at RT and 9.2% at 77 K have been achieved.[3]

One of the aims of the work reported here was to assess the microstructure and chemical distribution of junctions prepared using the multiple oxidation method, using high spatial resolution electron microscopy techniques and contribute towards an understanding of how the atomic states close to the junction area contribute to the spin tunneling process as the need for such information is deemed essential for theoretical calculations.[4]

II. SAMPLES AND TECHNIQUES

Three types of /Nb/Fe/Al_2O_3/CoFe junctions fabricated by sputter deposition, with different numbers of extra Al_2O_3 barrier layers were investigated. The base Al_2O_3 barrier layer was prepared by depositing a layer of Al (around 1 nm) and oxidizing it in 1 kPa O_2 for 10 min. Further 0.1 nm thick Al layers were then deposited and oxidized at the same time. The junctions analyzed were designated PKX (X=0, 1, 3), where X is the number of extra Al layers. For further details of how the junctions were prepared see Refs. 3 and 5. The room temperature JMR plotted against the applied magnetic field for these three junctions can be seen in Fig. 1. PK3 has the highest JMR (6.2%) followed by PK1 (2.3%) and then PK0 (1.4%).

The microscopy and analysis were performed on two differently configured microscopes. The energy dispersive x-ray (EDX) mapping was performed on a VG HB501 dedicated scanning transmission electron microscope (STEM) with a windowless EDX detector. High resolution electron microscopy (HREM) and electron energy loss imaging (EELI) and spectroscopy (EELS) experiments were performed using a JEOL 3000F field emission gun TEM (FEGTEM) with a Gatan imaging filter (GIF).

III. MICROSTRUCTURAL INVESTIGATIONS

A HREM image of the barrier region of PK1 (one extra Al layer) can be seen in Fig. 2. Metallic layers with the

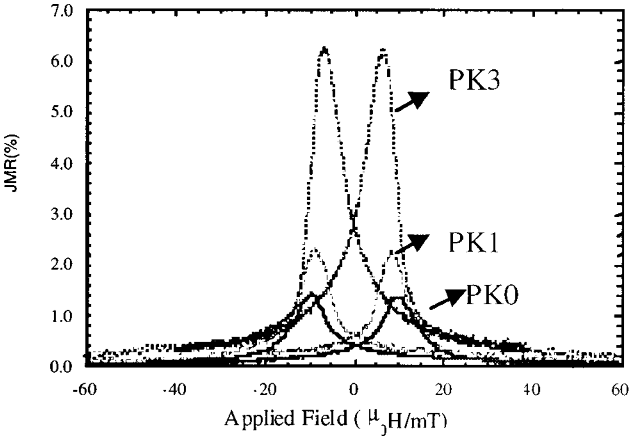

FIG. 1. Room temperature JMR plotted against the applied magnetic field for Fe/Al_2O_3/CoFe junctions with 0, 1, and 3 extra oxidized 0.1 nm wide Al layers in the barrier.

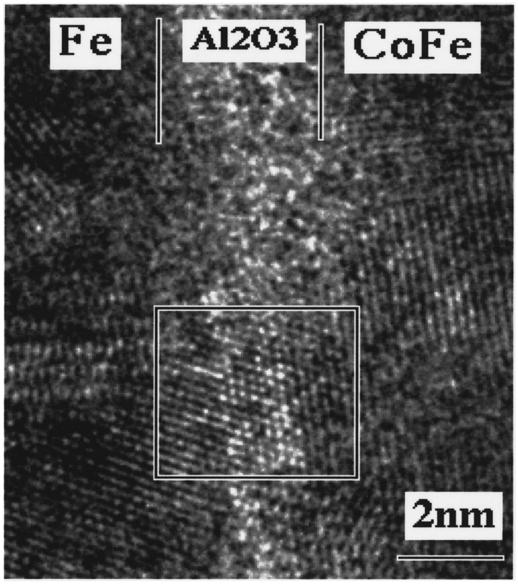

FIG. 2. HREM image of the barrier region of sample PK1. A marked box shows a region of crystalline continuity across the barrier where a pinhole has formed.

crystalline structure can be seen on either side of an amorphous Al-oxide barrier. Amorphous material is distinguishable by random speckle contrast. This image shows that the junction barrier has an uneven layer width (2.5–3.5 nm). A marked square box shows an area of continuous crystalline structure across the barrier layer. Analysis of the crystalline region suggests that it is an Fe grain that has extended across the barrier, as opposed to an unoxidized region of Al and this will form a pinhole, across which most of the current leakage will occur. Along an area of 500 nm investigated there were around three pinholes. In sample PK3, no clear pinholes were observed in the part of the sample examined, which may be due to lesser density of pinholes along the barrier of this sample. This shows itself as increased magnetoresistance in this sample (6.5%) compared to PK1 (2.3%). The modeling of the magnetoresistance of these samples[3] predicted the densities of pinholes necessary for the corresponding drop in magnetoresistance from Julliere's model[6] (around 40% JMR Ref. 3). Moreover, in PK3 the barrier layer was again very uneven in width and wider than intended. To approach the theoretical JMR values given by Julliere's model for the Fe/Al_2O_3/CoFe spin tunnel system would require larger areas of constant barrier layer width.

A bright field image and electron energy loss elemental maps from sample PK1 are shown in Fig. 3. The elemental distribution profiles obtained from individual maps are also shown. The Fe map has the highest signal to noise ratio for the maps shown here, and details such as the wavy nature of the barrier/ferromagnet can be resolved. The Al map suffers from inferior statistics because the Al K edge (1560 eV) is at a high energy loss. The O map shows an oxygen-depleted region near the Fe layer which is more clearly distinguished in the intensity profile. This has clear implications for the junction as unoxidized Al sites along the edge of the barrier adversely influence the spin tunneling properties.

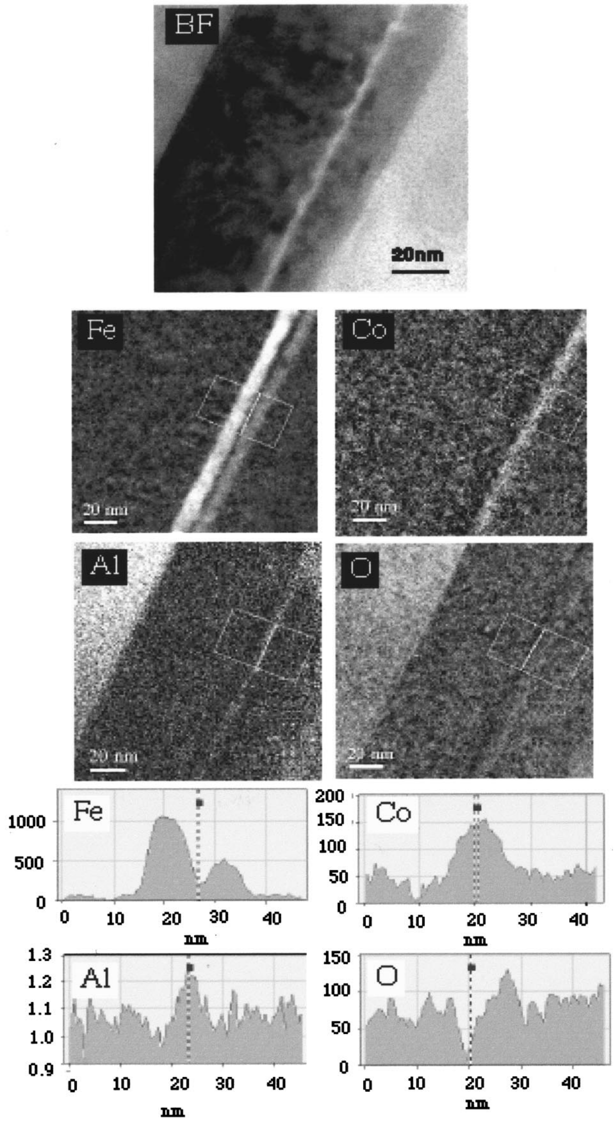

FIG. 3. Bright field image, EELS elemental maps, and intensity profiles from the marked areas of maps in sample PK1.

Figure 4 shows a set of background subtracted EELS spectra taken across the PK1 junction. The position of the various layers is indicated in the figure. The stepping distance between adjacent spectra is approximately 1.5 nm. The initial beam position was at the Nb/Fe interface and the final position was at the CoFe/Nb interface. The visible edges are O K (532 eV), Fe $L_{2,3}$ (712 eV), and Co $L_{2,3}$ (779 eV) (the Nb edges are not within this energy range). As the beam moves towards the Fe layer, the Fe $L_{2,3}$ edge starts to appear. At this stage no O K edge is visible indicating the absence of surface oxide layer. Near the barrier layer the O K edge starts to appear and the shape of the Fe $L_{2,3}$ edge changes sharply, with the Co $L_{2,3}$ edge appearing as the CoFe layer is approached. The changes in edge shape along the line indicate differences in the *d*-band occupancies for both Fe and Co, which are a result of changes in parameters such as oxidation state, magnetic moment or spin polarization of the Fe and CoFe layers. For example, the abrupt change in jump ratio for the Fe edge may arise from partial oxidation of the Fe layer close to the Al_2O_3 barrier layer which will lead to a

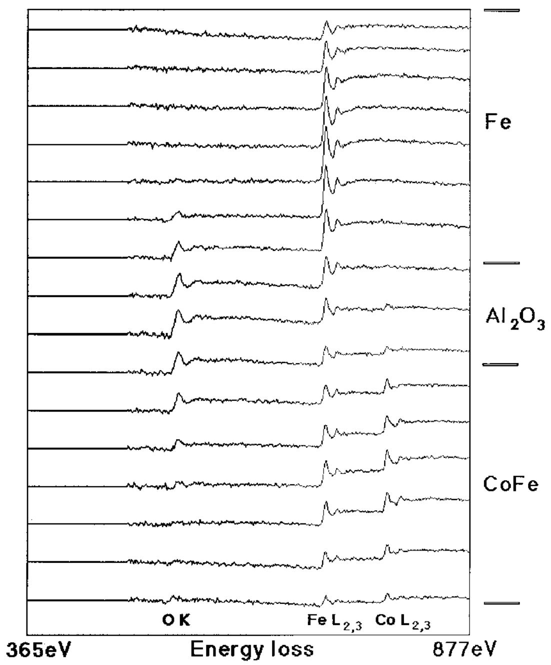

FIG. 4. Background-subtracted EELS spectra acquired across the barrier showing changes in O K, Fe L, and Co L edge characteristics.

change in spin polarization and thus in the JMR ratio. Quantitative analysis of this data is currently being undertaken, using the technique described in Ref. 7 to extract the d-band occupancies from the EELS spectra. This technique therefore provides an experimental means whereby variations in d-band occupancy on the atomic scale can be measured, which can then be included in theoretical models of the spin-tunneling effect.

IV. SUMMARY

A microstructural investigation of spin-tunnel junctions with multiply-oxidized barriers has been carried out. The investigation revealed the presence of pinholes that are probably the main reason for the lower than expected JMR ratios. High spatial resolution EELS composition mapping has indicated areas of incomplete Al oxidation and waviness of the barrier layer. EELS spectra recorded across the junction layers showed significant changes in the Fe and Co $L_{2,3}$ edges which indicate partial oxidation of the Fe and CoFe layers, leading to variations in magnetic moment and spin polarization which would need to be taken into account in theoretical predictions.

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