Layer and interface structural changes in Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$/AlO$_x$ multilayers on annealing

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Sputtered multilayers of Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$ and AlO$_x$ have been measured using grazing incidence x-ray scattering to determine the changes in layer and interface structure during in situ annealing. We confirm our earlier deduction of a sharpening of the interfaces on annealing up to 400 °C. This sharpening arises from reduction in chemical intermixing, not from change in topological roughness and provides an explanation for the enhanced tunneling magnetoresistance. The annealing is shown to result in a decrease in Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$ mean layer thickness and increase in the layer density. There is a commensurate increase in AlO$_x$ mean layer thickness while at the same time there is a reduction in the layer density. The increase in thickness could explain the corresponding increase observed in the resistance-area product. © 2010 American Institute of Physics. [doi:10.1063/1.3366707]

I. INTRODUCTION

In magnetic tunnel junctions (MTJs), where electrons tunnel through a nanometer-scale insulating barrier between ferromagnetic electrodes, there is a continuing quest to increase the fractional change in the junction resistance (called the tunneling magnetoresistance or TMR) when the magnetization of the electrodes is switched from parallel to antiparallel. Despite the large amount of work in progress on MTJs with MgO barriers and amorphous CoFeB electrodes, there is a continuing quest to increase the fractional change in the junction resistance.

The spin polarization required for TMR operation has been shown to be highly influenced by the electronic and structural nature of the interfaces and thus it is crucial for the optimization of device performance that the interface growth be under precise control. It is believed that the addition of boron improves the perfection of the interfaces by creating an amorphous structure that does not replicate the crystalline grain growth from the layer underneath.

A low temperature annealing stage in the manufacturing process is regularly used to enhance the TMR of MTJ devices. We have previously reported experiments showing that in the annealing process, used to maximize the TMR without pushing the resistance-area product unacceptably high, the interface between the alumina barrier and bottom CoFeB electrode reduces in width, there being no change in topological roughness. As the grazing incidence x-ray scattering experiments were conducted on partial device structures, this conclusion of chemical sharpening arose from detailed modeling of complex reflectivity profiles. In this paper, we report similar in situ annealing experiments on simplified periodic multilayer structures. Despite the risk that the interface perfection may degrade as the repeated number of layers increases, the modeling and interpretation of the x-ray reflectivity and diffuse scatter can be achieved with much greater confidence. In particular, Bragg sheets appear in reciprocal space associated very specifically with the conformal roughness of the interfaces.

II. EXPERIMENTAL DETAILS

Samples were prepared in Erlangen by magnetron sputtering on plasma-etched, thermally oxidized Si wafers. The nominal layer structures were [Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$(3 nm)/AlO$_x$(1.2 nm)]$_5$. Base pressure in the sputter system is in the range of 4×10$^{-8}$ mbar and the Ar sputter gas pressure was set to 5 μbar. Sputtering of the magnetic and dielectric layers was performed in dedicated sputter chambers, to prevent cross-contamination. Before deposition of the layer stack the substrate was precleaned by plasma etching for 15 min. Whereas each of the 3 nm thick CoFeB layers is made out of a multiple of 20 sublayers by subsequently rotating the substrate across the target (2 rpm), the 1.2 nm aluminum layer is deposited in a single run (3.5 rpm). Afterwards the aluminum is oxidized in a plasma process using Ar/O$_2$(5%) sputter gas at a pressure of 10 μbar. This process of sputter-etching, where the argon in the plasma etches into the aluminum and the aluminum is oxidized at the same time results in the stoichiometry being governed by the ratio of argon to oxygen in the plasma, and the length of time the plasma is applied to the sample. As the stoichiometry is not exactly Al$_2$O$_3$, the material is referred to as AlO$_x$. The thickness of the aluminum oxide is typically 30% more than that of the Al originally deposited. An increase in thickness of approximately two has been previously observed following glow discharge oxidation.

High resolution grazing incidence x-ray scattering experiments were performed at the, now closed, SRS synchrotron radiation source at Daresbury Laboratory. In situ reflectivity measurements were made during annealing in a high temperature annealing stage.
purity argon atmosphere slightly above atmospheric pressure. The chamber was carefully flushed through with argon before measurements were taken. Heating was by the induction furnace on station 2.3 using alignment and data collection techniques that are standard to all such measurements. To maximize the intensity from the bending magnet, a wavelength $\lambda$ of 0.13 nm was selected from the channel-cut 111 Si crystal monochromator. Specular and diffuse x-ray scatter was fitted to model structures using the BEDE REFS software package.\(^{12}\)

### III. RESULTS

#### A. As-grown structures

An example of the specular and off-specular scatter from a typical sample is shown in Fig. 1. Good agreement between experimental and simulated curves could be obtained only when the interface width was assumed to increase systematically through the stack. The parameters used in Fig. 1 are given in Table I, together with the statistical precision on the layer thickness and interface width values. (We note that the electron density of the Si substrate and the thermal oxide layers of polycrystalline Co/Pd are too small to detect any effect of this interface in the reflectivity curves and the thickness of the oxide is taken as infinite.) The variation in the fitted value for layer thickness through the multilayer is greater than the statistical precision in the fit. This is probably a result of cross-correlation of parameters when searching for the global minimum in the difference between simulated and experimental curves. There is no systematic variation in thickness through the stack.

![Fig. 2. Interface width as a function of repeat number.](image)

Careful fitting of the specular reflectivity to the data revealed that the interface width of the $\text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2}$ on $\text{Al}_2\text{O}_3$ interfaces was lower than that of the $\text{Al}_2\text{O}_3$ on $\text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2}$ interfaces, both interface widths increasing linearly with repeat number at the almost the same rate (Fig. 2). The topological roughness and interdiffusion profile cannot be separated from measurement of the specular scatter alone, as the electron density profile is sampled only in the direction normal to the surface. However, measurement of the off-specular scatter enables the two effects to be distinguished. We observed that the off-specular scatter is low. By fitting simulations from a model structure to the data (Fig. 1), we found that the best-fit topological roughness was 0.055 nm and thus responsible for only about 10% of the interface width. We note that the increase in the total interface width with multilayer repeat (Fig. 2) is greater than the topological roughness. As the intermixing width and topological roughness add in quadrature, the observed increase in total interface width must therefore arise from increased chemical intermixing at the interfaces, not an increase in topological roughness.

The roughness amplitude is determined by the amount of diffuse scatter; the distribution of diffuse scatter is determined by the in-plane roughness parameters. Simulation of the rocking curve with the parameters used to fit the off-specular scan of Fig. 1 shows an excellent fit to the experimental data (Fig. 3). The fractal parameter of 0.7 corresponds to a fractal dimension of 2.3 and the in-plane correlation length of 100 nm of these amorphous systems is long compared, for example, with low repeat number multilayers of polycrystalline Co/Pd (Ref. 13) or ultra-high vacuum evaporated Co/Cr trilayers.\(^{14}\) We also note that the out-of-plane correlation length of the roughness is long com-

#### Table I. Layer thickness, fractional density, and interface width.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Density of bulk (%)</th>
<th>Interface width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$2.029 \pm 0.048$</td>
<td>80.0 $\pm$ 6.1</td>
<td>0.510 $\pm$ 0.016</td>
</tr>
<tr>
<td>9</td>
<td>$\text{Co}<em>{0.6}\text{Fe}</em>{0.2}\text{B}_{0.2}$</td>
<td>$1.783 \pm 0.038$</td>
<td>84.2 $\pm$ 2.3</td>
<td>0.567 $\pm$ 0.028</td>
</tr>
<tr>
<td>8</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$1.704 \pm 0.024$</td>
<td>85.0 $\pm$ 5.0</td>
<td>0.481 $\pm$ 0.021</td>
</tr>
<tr>
<td>7</td>
<td>$\text{Co}<em>{0.6}\text{Fe}</em>{0.2}\text{B}_{0.2}$</td>
<td>$1.796 \pm 0.040$</td>
<td>85.0 $\pm$ 2.7</td>
<td>0.515 $\pm$ 0.023</td>
</tr>
<tr>
<td>6</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$1.943 \pm 0.026$</td>
<td>80.0 $\pm$ 5.2</td>
<td>0.454 $\pm$ 0.015</td>
</tr>
<tr>
<td>5</td>
<td>$\text{Co}<em>{0.6}\text{Fe}</em>{0.2}\text{B}_{0.2}$</td>
<td>$1.871 \pm 0.023$</td>
<td>82.7 $\pm$ 2.9</td>
<td>0.500 $\pm$ 0.020</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$1.851 \pm 0.033$</td>
<td>80.7 $\pm$ 6.1</td>
<td>0.434 $\pm$ 0.015</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Co}<em>{0.6}\text{Fe}</em>{0.2}\text{B}_{0.2}$</td>
<td>$1.860 \pm 0.025$</td>
<td>80.0 $\pm$ 4.0</td>
<td>0.484 $\pm$ 0.021</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$1.836 \pm 0.026$</td>
<td>85.0 $\pm$ 9.9</td>
<td>0.409 $\pm$ 0.02</td>
</tr>
<tr>
<td>1</td>
<td>$\text{Co}<em>{0.6}\text{Fe}</em>{0.2}\text{B}_{0.2}$</td>
<td>$1.860 \pm 0.024$</td>
<td>81.2 $\pm$ 7.8</td>
<td>0.392 $\pm$ 0.026</td>
</tr>
<tr>
<td>Substrate</td>
<td>$\text{SiO}_2$</td>
<td>$\infty$</td>
<td>98.8 $\pm$ 30.3</td>
<td>0.332 $\pm$ 0.016</td>
</tr>
</tbody>
</table>

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pared with the total multilayer stack thickness. To a good approximation, the roughness is conformal throughout the stack.

**B. Effects of annealing**

On annealing, the most noticeable change was in the height of the third order Bragg peak, which increased systematically with temperature (Fig. 4). With the assumption of a linear variation in interface width, we were able to obtain similar quality fits to that at room temperature between simulation and experiment for all temperatures during the annealing process (Fig. 5). By such careful fitting of the whole reflectivity profiles, we have determined the average width of both \( \text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2} \) on \( \text{Al}_2\text{O}_3 \) interfaces and \( \text{Al}_2\text{O}_3 \) on \( \text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2} \) interfaces as a function of annealing temperature. Both fell linearly with temperature (Fig. 6) though at different rates for the two types of interface. Measurement of the diffuse x-ray scatter showed that the topological roughness of the multilayer interfaces remained of constant amplitude and no changes were found for the in-plane length scale of the roughness. The reduction in interface width therefore arises from a sharpening of the chemical profile across the interfaces. This is consistent with our observations of the behavior of \( \text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2} / \text{Al}_2\text{O}_3 \) interfaces in the more complex MTJ structures.

Up to a temperature of approximately 250 °C, there was no significant change in the mean thickness of the layers outside of the measurement precision, but above this temperature, the \( \text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2} \) average layer thickness decreased, while the average \( \text{Al}_2\text{O}_3 \) thickness correspondingly increased (Fig. 7). At the same time, the average \( \text{Co}_{0.6}\text{Fe}_{0.2}\text{B}_{0.2} \) layer density increased by about 3%, while the average density of the \( \text{Al}_2\text{O}_3 \) layers showed a small decrease in about 1% (Fig. 8). While these values are not outside of the errors bars associated with the fitting procedure, there is, in both cases, an evident systematic trend in best-fit values.

**IV. DISCUSSION**

The diffuse x-ray scatter measurements confirm and quantify transmission electron microscopy measurements of
the low value of the roughness amplitude in the Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$/AlO$_x$ system.\cite{15} It is generally accepted that this arises because of the absence of grains and the associated boundaries in these amorphous materials. A new observation is that the interface width increases with multilayer repeat, while there is no substantial increase in the topological roughness. All models of film growth predict an increase in roughness amplitude with increasing film thickness, the scaling exponent depending on the growth mechanism,\cite{16} and our own simulations of multilayer growth using both ballistic and random deposition with surface relaxation models confirm this behavior.\cite{17} However, the constancy of topological roughness with layer number in our best-fit simulation does not invalidate this description, as the experiment is ill-conditioned to extract these data. What is clear, nevertheless, is that the absolute value of the topological interface roughness is small compared with the total interface width and thus no gradient in topological roughness can account for the increase in total interface width. The reason for this increase in chemical intermixing with repeat number is not immediately obvious but could possibly arise from transfer of material through pinholes, which are known to exist in alumina tunnel barriers of this thickness.\cite{18} Such a mechanism could account for the low value of the interface width, apparent in Fig. 2, between the first AlO$_x$ layer and the first CoFeB layer compared with the subsequent AlO$_x$ on CoFeB interfaces. The first AlO$_x$ layer will have been deposited on a pinhole-free CoFeB layer, there thus being less material transport and a lower interface width. The amorphous nature of the films probably lies behind the almost two-dimensional nature of the interface, there being significantly less high frequency components to the in-plane roughness than in polycrystalline films.

Interface widths in the multilayer structures are very close to those previously measured in MTJ structures containing only a single alumina barrier and additional materials in the stack.\cite{7} The decrease in interface width with annealing temperature is also very similar to the values deduced previously by a reverse modeling of a single feature in the complex reflectivity profile of the MTJ structure.\cite{7} There is no doubt that the interface intermixing does reduce substantially during the annealing sequence. We observed some time ago that the width of the interface between Co and Al reduces when the Al is oxidised,\cite{19} implying that the chemical potential is reduced by migration of the Al to form the oxide. It appears that this process is not complete and that on annealing there is additional movement of atoms, probably of Al to move the oxide composition closer to stoichiometry. Such a presumption is consistent with the increase in thickness of the alumina barrier with annealing temperature (Fig. 7).

Sharpening of the interface could be the structural change responsible for the increased TMR on annealing Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$/AlO$_x$ MTJs.\cite{6,15} Calculation of the spin-dependent tunneling in epitaxial MgO/Fe junctions\cite{20} reveals that interface disorder significantly reduces the TMR and by implication, reduction in interface intermixing width should also enhance the spin coherence in the amorphous system. However, associated with the increased TMR on annealing is also a rise in the resistance-area product. As the tunneling resistance is an exponential function of barrier thickness, a small change in barrier width can result in a substantial change in resistance. The thickness of an MTJ barrier is chosen to optimize the conflicting requirement of high TMR and minimal resistance, required to reduce noise. There is a small increase in alumina barrier thickness at the higher annealing temperatures which may be responsible for the increase in resistance-area product observed above about 300 °C.\cite{5}

The reduction in alumina barrier density may be associated both with a change in stoichiometry, from the reduction in interface width, and the conservation of material necessary upon increase in the barrier thickness. Increase in density of the Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$ layers is consistent with conservation of material upon decrease in Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$ layer thickness.

V. CONCLUSIONS

Grazing incidence x-ray scattering measurements have confirmed that annealing of Co$_{0.6}$Fe$_{0.2}$B$_{0.2}$ and AlO$_x$ films results in reduction in the chemical intermixing at the interface, the values of the changes being consistent with earlier, less directly interpretable, measurements. This reduction provides a possible mechanism for the well established increase.
in TMR obtained when tunnel junctions are annealed. The increase in resistance-area product on annealing may be related to the observed increase in thickness of the alumina layers.

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