Enhanced magnetoresistance in naturally oxidized MgO-based magnetic tunnel junctions with ferromagnetic CoFe/CoFeB bilayers

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Three-dimensional elemental distributions in magnetic tunnel junctions containing naturally oxidized MgO tunnel barriers are characterized using atom-probe tomography. Replacing the CoFeB free layer (reference layer) with a CoFe/CoFeB (CoFeB/CoFe) bilayer increases the magnetoresistance from 105% to 192% and decreases the resistance-area product from 14.5 to 3.4 Ω μm². The CoFe/CoFeB bilayer improves the compositional uniformity within the free layer by nucleating CoFeB crystals across the entire layer, resulting in a homogeneous barrier/free layer interface. In contrast, the simple CoFeB free layer partially crystallizes with composition differences from grain to grain (5–30 nm), degrading the tunnel junction performance. © 2011 American Institute of Physics. [doi:10.1063/1.3597224]

Magnetic tunnel junctions (MTJs) utilizing MgO tunnel barriers are the subject of intense research due to the large tunneling magnetoresistance (TMR) effect that they exhibit.1–3 This effect is vital in the data-storage industry for read sensors in hard-disk drives and for memory elements in nonvolatile magnetic random access memory.1 Transmission electron microscopy (TEM) studies demonstrate that the crystalline microstructure of a MTJ strongly affects its magnetotransport properties.4–7 The role of atomic-level elemental distributions are, however, more difficult to probe directly.8,9 Particularly, the role of the B distribution within CoFeB/MgO/CoFeB MTJs (Ref. 10) is extremely difficult to detect. Atom-probe tomography (APT) (Refs. 11–13) is an analytical technique capable of analyzing three-dimensional (3D) elemental distributions, including that of B within CoFeB-containing MTJs.9,14

It has recently been demonstrated that a large TMR effect can be realized in naturally oxidized MgO tunnel barriers by replacing CoFeB with bilayers of CoFe/CoFeB.15,16 This is significant as high TMR values are generally observed only for rf-sputter deposited MgO, which has limited industrial applicability due to problems inherent to the deposition technique (particle generation, poor uniformity control, and low throughput). MgO growth using dc magnetron deposition of metallic Mg followed by oxidation permits higher yield and broader applicability. We employ APT to reveal the role of the 3D elemental distributions on the resulting TMR ratio, resistance-area (RA) product and magnetization reversal in naturally oxidized MgO-based MTJs containing either single-layer CoFeB or bilayer CoFe/CoFeB ferromagnetic layers.

Model MTJs were deposited on high-conductivity Si substrates: Si/Seed/PtMn(20)/PL/Ru(0.85)/RL/MgO(1.2)/FL/Ru(1)/Cap(80) (thicknesses in nanometer). The standard stack comprised: pinned layer (PL)=Co70Fe30(2.5); reference layer (RL)=Co80Fe20B20(3); and free layer (FL)=Co60Fe20B20(8). For the bilayer stack the comparable bilayers were: PL=Co60Fe20B20(1.5)/Co80Fe20(3); RL=Co60Fe20B20(1.5)/Co90Fe10(1.5); and FL=Co70Fe30(1.5)/Co90Fe10B20(6.5). The RL and FL compositions of the bilayer stack were optimized previously.15 The cap [Co(15)/Fe(65)] served as a sacrificial layer during APT sample preparation. The metallic layers were deposited by dc magnetron sputtering. MgO was grown by depositing 0.8 nm of Mg via dc magnetron sputtering, followed by natural oxidation (pure oxygen) at flow rates of 700 and 1000 s.c.c.m. for 1200 and 120 s for the standard and bilayer stacks and lastly deposition of 0.3 nm of Mg. Samples were annealed for 2 h at 380 °C in a 10 kOe in-plane magnetic field. Separate samples having identical MTJ stacks and additional electrode layers were grown for magnetotransport and magnetic hysteresis measurements via current in-plane tunneling (CIPT) and vibrating sample magnetometry (VSM).17 APT specimens were prepared by focused ion-beam lift-out and shaped using 30 and 5 kV Ga⁺ ions to an end diameter of ~80 nm.18 APT analyses were performed using laser pulsing (λ=355 nm; laser energy ∼0.04 nJ pulse⁻¹) at a base temperature of <50 K.12,13 Reconstructions were made from the central ~10–30 nm tip diameter to minimize spatial aberrations from multilayer field evaporation (Ref. 19) and avoid Ga⁺ ion-beam damage.

CIPT and VSM measurement results are displayed in Table I. The standard stack has a TMR value of 105%, and RA product of 14.5 Ω μm². The bilayer stack has a higher TMR value of 192% and a smaller RA product of 3.4 Ω μm². Both samples exhibit an exchange bias of ~1200 Oe. The synthetic antiferromagnet (SAF) plateau is more stable for the bilayer stack (510 Oe) than for the standard stack (270 Oe). It has been suggested (Refs. 15 and 20) that B at the PtMn/PL interface inhibits the diffusion of Mn to the Ru layer, thereby improving the SAF plateau...
stability,21 APT analysis, Table I, reveals that 10–13 at. % B segregates at the PtMn/PL interface in both samples without measurable Mn diffusion. Note that the B in the standard stack diffuses from the CoFeB RL to the PtMn/CoFe interface, whereas the B in the bilayer stack is present at the PtMn/CoFeB interface prior to annealing. Ru segregates at the PtMn/CoFe interface at up to 4 ± 1 at. % in the standard stack, but only ~1 at. % Ru in the bilayer stack. APT analyses of both samples before annealing (data not shown) revealed no Ru segregation. We suggest that the diffusion of Ru in the standard stack is aided by the diffusion of B from the RL to the PtMn/PL interface. This does not occur in the bilayer stack since B segregates prior to annealing. The reduced diffusion of Ru improves the strength of the SAF interlayer exchange coupling in the bilayer stack.

Representative APT reconstructions of the MgO/FL/Ru region are displayed in Fig. 1. Detected atoms of Fe, Mg, Ru, and B are displayed and all others are omitted. An 8 at. % B isoconcentration surface (Ref. 22) (blue ribbon) delineates regions of high- and low-B concentration. The B distribution in the standard stack, Fig. 1(a), is inhomogeneous. The B isoconcentration surface dissect the CoFeB FL, separating a B-rich grain (left) from a B-poor grain (right). The bilayer stack, Fig. 1(b), shows no delineation of B-rich and B-poor grains. Instead, the CoFe/CoFeB FL contains <8 at. % B, while the top 1 nm of the bilayer contains >8 at. % B. This indicates that B has diffused toward the Ru FL cap, but has not completely partitioned to the Ru layer. Small concentrations of B (1–2 at. %) decorate grain boundaries in the Co cap, suggesting that some B diffuses out of the tunnel junction.

One-dimensional (1D) concentration profiles from two grains of the standard stack, marked 1 and 2 in Fig. 1(a), are plotted in Fig. 2. The B-rich grain, Fig. 2(a), has a concentration of ~12–15 at. % B throughout the layer, while the B-poor grain, Fig. 2(b), contains only 1–3 at. % B. Within this B-poor region the B concentration increases to ~12 at. % and ~5 at. % at the CoFeB/Ru and MgO/CoFeB interfaces, respectively. Boron diffuses out of CoFeB during crystallization, thus region 1 in Fig. 1(a) is probably an amorphous grain that has not crystallized while region 2 is a crystalline grain. The increased B at the interfaces of region 2 with MgO and Ru suggests a locally disordered crystal structure. This hypothesis is confirmed by energy-filtered TEM mapping of the B distribution in amorphous and crystalline grains of the FL (data not shown), which indicates that the crystalline grains are depleted of B, while the amorphous grains retain a significant amount of B. The CoFe composition varies between the two grains with the B-rich grain exhibiting a Co:(Co+Fe) ratio of 0.86 ± 0.01, while the B-poor grain exhibits a ratio of 0.70 ± 0.01, suggesting that diffusion of B is accompanied by diffusion of Fe toward the crystallized grains. A representative 1D concentration profile through the bilayer stack FL is displayed in Fig. 3. The B

![FIG. 1.](Image 333x51 to 525x161) (Color online) APT reconstruction (~5 nm thick slice) of the MgO/FL portion of: (a) the standard stack and (b) the bilayer stack. An 8 at. % B isoconcentration surface (blue ribbon) delineates regions of high and low B concentration. The cylinders labeled 1 and 2 in panel (a) correspond to regions from which concentration profiles are taken from adjacent grains (see Fig. 2).

![FIG. 2.](Image 333x548 to 525x743) (Color online) 1D concentration profiles for (a) B-rich grain (region 1) and (b) B-poor grain (region 2) within the CoFeB FL of the standard stack. Error bars from counting statistics (one standard deviation) are displayed for Fe.

![FIG. 3.](Image 70x89 to 262x256) (Color online) 1D concentration profile of the CoFe/CoFeB FL in the bilayer stack.

**TABLE I.** Magnetic and magnetotransport properties of the standard stack and bilayer stack samples after annealing at 380 °C for 2 h. The segregation of B and Ru at the PtMn/PL interface measured by APT are also displayed.

<table>
<thead>
<tr>
<th></th>
<th>Standard stack</th>
<th>Bilayer stack</th>
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<tbody>
<tr>
<td>TMR (%)</td>
<td>105</td>
<td>192</td>
</tr>
<tr>
<td>RA (Ω·µm²⁻¹)</td>
<td>14.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Exchange Bias (Oe)</td>
<td>1130</td>
<td>1310</td>
</tr>
<tr>
<td>SAF Plateau (Oe)</td>
<td>270</td>
<td>510</td>
</tr>
<tr>
<td>B Segregation (at. %)</td>
<td>10.2 ± 1.2</td>
<td>13.0 ± 0.8</td>
</tr>
<tr>
<td>Ru Segregation (at. %)</td>
<td>3.9 ± 0.8</td>
<td>1.3 ± 0.3</td>
</tr>
</tbody>
</table>
distribution is laterally uniform, with a concentration between 1–3 at. % B that increases to ~5 at. % and ~15 at. % at the MgO/FL and FL/Ru interfaces, respectively. This B distribution is similar to that found in the crystallized region of the standard stack. The Fe-rich composition of the Co$_{95}$Fe$_{50}$ sublayer is preserved after annealing and no significant lateral variations in the Co:(Co+Fe) ratio exist.

Differences in elemental distributions affect the magnetotransport properties of the MTJs. For the standard stack, partial crystallization of the CoFeB FL and RL leads to the presence of B-rich amorphous grains and B-poor crystalline grains. Amorphous CoFeB exhibits poor magnetotransport characteristics due to the absence of lattice matching between the electrode and tunnel barrier. This limits the cross-sectional area of the interface in the standard stack that can exhibit coherent tunneling, which is required for a high TMR value. The concentration of Fe also varies for each grain, leading to nonuniform magnetic properties along the FL. In contrast, the bilayer stack is uniformly crystalline, leading to uniform magnetic properties and a large cross-sectional area for coherent tunneling. The crystalline CoFe layer deposited adjacent to the MgO acts as a crystallization template, improving the overall crystallinity of the CoFeB after annealing and thus the TMR of the MTJ. The concentration of B at the MgO/FL interface is equivalent (~5 at. %) for the crystalline regions of the standard and bilayer stacks, which suggests that small concentrations of B at the MgO/FL interface do not reduce drastically the TMR value of the MTJ, in agreement with other studies. Higher B concentrations at the MgO/FL interface are observed in the amorphous regions of the standard stack, which could lead to the presence of more B-oxide and explain partially the higher RA product of the standard stack.

In summary, MTJs containing naturally oxidized MgO tunnel barriers exhibit higher TMR values and lower RA products when bilayers of CoFeB/CoFe replace the standard CoFeB layers. The bilayers crystallize uniformly upon annealing and form a continuous crystalline FL, in contrast to the partial crystallization exhibited by CoFeB FL. The bilayer CoFeB/CoFe FL has a larger cross-sectional area for coherent tunneling, providing a larger TMR value at a smaller RA product. A CoFeB/CoFe PL bilayer also exhibits greater SAF thermal stability in comparison to a standard CoFe PL by inhibiting the diffusion of B and Ru through the PL to the PtMn/PL interface.

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