Spatially resolved electron energy-loss spectroscopy of electron-beam grown and sputtered CoFeB/MgO/CoFeB magnetic tunnel junctions

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Electron energy-loss spectroscopy at subnanometer resolution is used to investigate CoFeB/MgO/CoFeB magnetic tunnel junctions grown by electron-beam evaporation and radio frequency (rf) sputtering before and after annealing. Gap states were observed in the MgO layer for both growth methods although the rf-sputtered MgO layer showed significantly more gap states. Asymmetry in oxygen bonding between the top and bottom CoFeB/MgO interfaces was also observed. Moreover, significant amounts of diffused B as BO₂ were observed in the rf-sputtered MgO layer. A Mg underlayer between the MgO layer and the bottom electrode greatly reduced BO₂ formation in the barrier upon annealing. © 2007 American Institute of Physics.

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Magnetic tunnel junctions (MTJs) with a MgO tunnel barrier have attracted great interest as memory devices since the prediction of a high tunneling magnetoresistance (TMR) for epitaxially grown Fe/MgO/Fe MTJs.1,2 Ongoing studies of both epitaxially grown3 and sputtered4 MTJs have led to steady improvement in the TMR, up to 472% at room temperature in a recent demonstration.5 Yet, our understanding of what affects the TMR at an atomic level remains incomplete. For example, annealing the MTJs has been experimentally shown to increase the TMR.5,6 A proposed explanation is that annealing creates sharper interfaces and crystallizes the electrodes at the interface, which enhances the TMR.5,7,8 Conversely, annealing can promote diffusion of atoms in the MTJs,3 which may worsen the tunneling conductance of the barrier layer due to additional scattering terms introduced by the incorporation of foreign species in the barrier. Therefore, investigating the effects of annealing and of different growth methods on the MTJs at the atomic level is crucial to understanding how local chemical changes affect the TMR. Here, scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) with subnanometer resolution are used to examine MgO-based MTJs grown by the two most common deposition methods.

Electron-beam (e-beam) evaporation and radio frequency (rf) sputtering were used to grow 200 Å CoFeB/20 Å MgO (or 5 Å Mg/5 Å MgO)/200 Å CoFeB MTJs on thermally oxidized Si(100) substrates at a base pressure of ~2×10⁻⁹ Torr.9 The MTJs were studied as-grown as well as after a 1 h annealing at 375 °C. Although the investigated structures are not fully formed MTJ devices, they contain the essential electrode/buffer/electrode sandwich layers, which are sufficient for studying the local chemical profile in the MgO layer and at the MgO/CoFeB interfaces.

The MTJ structures were mechanically polished and ion milled in a wedge geometry for STEM experiments. The wedge geometry allows us to determine the effects of surface oxidations, which become a smaller and ultimately negligible fraction of the total signal as the projected thickness increases, provided the sample is transferred quickly from the mill to the microscope. Figure 1 shows TEM images of the e-beam grown and the rf-sputtered CoFeB/20 Å MgO/CoFeB structures (MgO[eb] and MgO[rf], respectively) and the rf-sputtered CoFeB/5 Å Mg/5 Å MgO/CoFeB structure (Mg/MgO[rf]) after annealing. The MgO[eb] layer shows the most crystallinity with sharp interfaces while the MgO[rf] layer contains many grain boundaries and rough interfaces. Lattice fringes are absent in the Mg/MgO[rf] bilayer, which implies that it is amorphous. As-grown structures show similar results with no obvious structural differences for all three cases.

For EELS studies, a 200 kV FEI Tecnai F20-ST STEM fitted with a monochromator and a Gatan imaging filter 685-ER was used. The electron beam was focused to form an ~2 Å diameter probe with a convergence semiangle of ~9.6 mrad. To reduce the electron dose per unit area for minimum radiation damage, EELS spectra were taken in a line parallel to the MgO/CoFeB interface. The spectrometer dispersion was set to 0.3 eV/channel to capture the wide energy range needed to record all edges simultaneously, resulting in an energy resolution of 1 eV.

FIG. 1. TEM images of annealed (a) e-beam-grown CoFeB/20 Å MgO/CoFeB, (b) rf-sputtered CoFeB/20 Å MgO/CoFeB, and (c) rf-sputtered CoFeB/5 Å Mg/5 Å MgO/CoFeB MTJ structure. Scale bars are 5 nm long.

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The fine structure of the O–K EELS edge provides information on the unoccupied O-p density of states and the local chemical environment surrounding O atoms\(^{10,11}\). Figure 2(a) shows the O–K edges of the bulk MgO, the MgO\([eb]\) layer, the MgO\([rf]\) layer, and the Mg/MgO\([rf]\) bilayer after annealing. Damping of the EELS extended fine structure is indicative of disorder or fewer surrounding O atoms\(^{10,11}\). The as-grown MgO\([rf]\) layer (not shown) is less ordered than the as-grown MgO\([eb]\) layer but after annealing [Fig. 2(a)], the O–K edge of the annealed MgO\([rf]\) layer follows that of the annealed MgO\([eb]\) layer closely, which indicates improved chemical ordering upon annealing. For the Mg/MgO\([rf]\) bilayer, the O–K edge has no resemblance to the bulk MgO O–K edge, which suggests that the bilayer has lost the characteristics of bulk MgO. Interestingly, the O–K edges of all the MgO layers are far from that of the bulk MgO even that after annealing, suggesting that even the 20 Å MgO layers are different from the bulk MgO.

A noticeable EELS signal (arrows in Fig. 2) is observed starting at 525 eV in the O–K preedge of the MgO\([eb]\) layer to indicate the presence of gap states which distinctly increase for the MgO\([rf]\) layer. Additionally, more gap states are observed at the interfaces than in the center of the MgO layer for both MgO structures. Because EELS reflects unoccupied density of states of a conduction band modified by a core hole effect,\(^{10-13}\) the appearance of the gap states can reflect band tailing in the conduction band of the MgO layer. Using a scanning tunneling microscope, Mather et al.\(^ {14}\) observed significant band tailing in the MgO/Fe structure, which was attributed to vacancies\(^ {15}\) and other structural defects.

Figure 2(b) and 2(c) show the O–K edges taken from the top and bottom CoFeB/MgO interfaces of the annealed MgO\([eb]\) and MgO\([rf]\) structures, respectively. Interestingly, the top and bottom interfaces exhibit distinctly different EELS spectra. For the MgO\([eb]\) structure, the bottom interface shows sharper features in the O–K edge and hence is more MgO-like than the top. This asymmetry could be due to the previously reported chemisorbed O species on the top surface of the MgO\([eb]\) layer.\(^ {14,16}\) Another possibility is the partial intermixing of the MgO\([eb]\) layer with the top electrode which was deposited using a dc magnetron sputtering.\(^ {9}\) Both effects would roughen the interface. For the MgO\([rf]\) structure, the bottom interface shows considerably more disorder than the bottom of the MgO\([eb]\) structure, and slightly more disorder than the top of the MgO\([rf]\) structure. This disorder is possibly from the oxidation of the bottom electrode by O ions released by the sputtering of MgO.\(^ {9,17}\) We would again expect some disorder in the top electrode of the MgO\([rf]\) structure due to chemisorbed O species or the partial intermixing during sputtering of the top electrode.

We use the B–K, Fe–L\(_2,3\), and Co–L\(_{2,3}\) edges to study the diffusion of atomic species across the MgO/CoFeB interfaces. Significant changes in the shape of the Co or Fe edges are not detected, which suggests that their chemical intermixing with the MgO is small. However, the B–K edge shows a dramatic change across the MgO layer. Figure 3 shows the B–K edges acquired from the electrode and from the center of the MgO layer of the three structures before and after annealing. The MgO\([eb]\) layer exhibits a low B–K signal [Figs. 3(a) and 3(b)], which indicates only a trace amount of B diffused from the electrode into the MgO\([eb]\) layer. For the as-grown MgO\([rf]\) layer [Fig. 3(c)], a significant B–K signal is observed, which suggests considerable B diffusion into the MgO layer, as found by previous XPS studies.\(^ {9}\) Moreover, the observed B–K edge displays a strong \(\pi^+\) peak at 193 eV characteristic of oxidized B in trigonal coordination with O.\(^ {18}\) This is in contrast to the metallic B in the electrode layers. Most of the BO\(_x\) remains in the barrier after annealing [Fig. 3(d)]. The situation for the Mg/MgO\([rf]\) bilayer is quite different. While BO\(_x\) is observed in the asgrown bilayer [Fig. 3(e)], after annealing, BO\(_x\) is not detected in the bilayer. Instead, the smaller B–K edge signal from the bilayer resembles that from the electrode [Fig. 3(f)]. There are likely two effects at play here: a genuine chemical change in the loss of the BO\(_x\) signal and an artifact of imaging a rough interface in projection in observing the metallic B signal. The total B–K signal found after annealing is less than that before annealing, which indicates that the B content in the bilayer has been reduced. The remaining B–K edge signal in the annealed bilayer structure has a metallic character that could be due to the presence of unoxidized B in the bilayer. However, considering the high affinity of B to O, the presence of unoxidized B seems unlikely. Instead, the metallic B–K edge signal is more likely to be the residual signal.
This view is supported by the observation that B remains and therefore change the B–O bonding configuration. This is a critical parameter in controlling the BO$_3$ content. The Mg/MgO bilayer structure. Annealing the structure reduces the BO$_3$ content slightly. Since high TMR values have been obtained with thick (≥2 nm) but not in thin (≈1 nm) MgO[rf] layers, this suggests either that some BO$_3$ content can be beneficial for TMR or that in those former cases the rf deposition or annealing protocol was sufficiently different from ours as to reduce the BO$_3$ content. With the Mg/MgO[rf] bilayer structure, BO$_3$ is observed in the as-grown bilayer but is dramatically reduced upon annealing. However, based on O–K edges, the annealed 5 Å Mg/5 Å MgO[rf] bilayer does not display MgO characteristics. A thicker Mg/MgO[rf] bilayer may recover MgO characteristics and reduce BO$_3$ even further via annealing. Asymmetry in O–K edges between the top and bottom interfaces observed for both the MgO[rf] and MgO[eb] structures may also affect the TMR by breaking the symmetry of the electrode/barrier/electrode junction structure.

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