Effects of annealing on local composition and electrical transport correlations in MgO-based magnetic tunnel junctions

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The effects of annealing on the electrical transport behavior of CoFe/MgO/CoFe magnetic tunnel junctions have been studied using a combination of site-specific in situ transmission electron microscopy and three-dimensional atom-probe tomography. Annealing leads to an increase in the resistance of the junctions. A shift in the conductance curve (dI/dV) minimum from 0 V for the as-grown specimen correlates with a sharply defined layer of CoFe oxide at the lower ferromagnetic interface. Annealing decreases the asymmetry in the conductance by making the interfaces more diffuse and the tunnel barrier more chemically homogeneous. © 2008 American Institute of Physics.

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Transport behavior in magnetic tunnel junctions (MTJs) is of great interest because of their unique magnetic properties and their potential for integration into a range of technological applications.1 In the simplest case, MTJs consist of a thin electrically-insulating layer sandwiched between two ferromagnetic electrodes. The resistance of the junction depends on the relative orientation of the magnetization in the two ferromagnetic layers. The tunneling magnetoresistance (TMR) ratio, which is directly proportional to the output signal of the device, is defined as the ratio of the difference in resistance when the magnetization of the electrodes are in the parallel versus antiparallel configuration, to the resistance in the parallel configuration. Theory predicts TMR ratios of up to 1000% or more for epitaxial MgO-based MTJs,2,3 but the current state-of-the-art experimental values reach only half that number.4 Despite their integration into magnetic read heads and magnetoresistive random access memory,5 to date many of the details of the magnetotransport properties, including the exact contribution of interfaces and defects, are not well understood.

It is well known that vacuum annealing can have a major effect on the magnetotransport properties of CoFe-based MTJs. Parkin et al.6 reported an increase in TMR with annealing temperature up to about 400 °C for sputter-deposited CoFe/MgO/CoFe MTJs that did not fail before reaching that temperature. The resistance of the functioning junctions, however, was found to change little over the same temperature range. This indicates that the mechanisms leading to an increase in TMR with annealing temperature are not necessarily the same as those that result in an increase in electrical resistance. An increase in spin polarization may be part of the reason for this observation: Wang et al.7 observed that annealing increases the spin polarization of a CoFe/MgO(001)/CoFe MTJ. Absolute temperature is not the only factor when considering the effects of annealing on MTJs, as it has been shown8 that optimal TMR values can be reached by annealing at lower temperatures for longer times. However the exact relationship has not been published in the literature.

In this article an analysis is presented on the effects of annealing on the local electrical transport behavior of sputtered CoFe/MgO-based MTJs using a recently developed in situ transmission electron microscopy (TEM) technique,9 which combines high spatial resolution imaging with site-specific transport characterization. A local-electrode atom-probe tomograph was employed to elucidate the chemical composition of the layers in three dimensions at sub-nanometer spatial resolution using atom-probe tomography (APT).10,11

Simple MgO-based MTJs were deposited onto boron-doped high conductivity Si(100) (ρ<0.001 Ω cm). The deposited layers were of the form Si substrate/Cr seed/Co50Fe50(5 nm)/MgO(2 nm)/Co50Fe50(10 nm)/Cr cap(60 nm). The metal films were grown by dc magnetron sputtering in 3 mTorr Ar. The MgO was deposited by reactive deposition of Mg metal in a background pressure of 10−5 Torr O2 to a nominal thickness of 2 nm. The MTJs were examined in the as-grown state and after annealing at 340 °C for 1 h in high vacuum (3.5×10−7 Torr). TEM specimens for in situ transport measurements were prepared using dual-beam focused ion-beam (FIB) milling with a final thickness in the direction of the electron beam of ~100 nm. The 60 nm thick Cr cap, which was sputter deposited during the initial film growth, acted as a protective metallization layer to prevent damage to the sample from Ga ions incident normal to the specimen surface. The FIB-induced damage that did occur is visible in the in situ TEM images collected at the transport measurement sites. Therefore, it is a part of the microstructure to be correlated with the transport data, and can be accounted for in the measurements. Current-voltage (I-V) characteristics were measured in situ in the TEM using a nanobiasing TEM holder, as described in detail elsewhere.9 A four-point probe dc method in the voltage

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sourcing mode was used; the probe tip was an electropolished gold wire with a final polished diameter of 100 nm, which was contacted within the specimen thickness and remained relatively constant in morphology and dimensions throughout the measurements. The variations due to contact resistance were therefore minimal. Variations in the I-V characteristics along the length of the barrier parallel to the layers are ascribed to differences in the barrier parameters, with the localization of the measurement attributed to ballistic transport. The source of ballistic electrons in this experiment is believed to be the very thin native oxide layer on the surface of the TEM specimen, which can be thought of as a tunnel barrier with negligible height that acts as a filter, blocking electrons with a strong transverse momentum component. Separate specimens suitable for high-resolution electron microscopy (HREM) were prepared by mechanical thinning followed by Ar$^+$ ion milling. The APT specimens were prepared using a FIB lift-out method. The APT analyses were performed employing picosecond laser pulsing at a specimen temperature of 60 K with a pulse repetition rate of 25 kHz.

Figure 1(a) displays site-specific I-V curves recorded in situ in the TEM, for both as-grown (●) and annealed (●) CoFe/MgO/CoFe MTJs. A decrease in the tunneling current at a given voltage, following annealing, indicates an increase in resistivity. An in situ TEM image of the as-grown specimen, recorded at the same position at which the as-grown I-V curve was measured, is shown in Fig. 1(b). The tunnel barrier exhibits light contrast and runs horizontally across the center of the image; it is sandwiched on either side by the CoFe ferromagnetic metal (FM) electrodes that exhibit darker contrast. The contrast within the tunnel barrier is non-uniform. There is a layer exhibiting intermediate contrast at the lower FM/MgO interface. By comparison, the in situ TEM image for the annealed specimen [Fig. 1(c)] displays more uniform contrast in the barrier. The local effective barrier height and width values were extracted from the experimental transport data by fitting to the Simmons model for tunneling through an insulating barrier. The Simmons model is an oversimplification and not necessarily phenomenologically accurate for rough barriers or local measurements; however, it naturally fits I-V characteristics, is simple, and is used here as a qualitative metric for comparison. Assuming the area of the junction is approximately equal to the square of the tip’s diameter, 100 nm, the average barrier heights and widths, respectively, are 1.6 V and 6.6 Å for the as-grown specimen and 1.3 V and 10.3 Å for the annealed specimen.

Figure 2 displays the conductance (dI/dV) curves calculated numerically from the I-V curves displayed in Fig. 1(a). The minimum of the dI/dV curve for the as-grown specimen is offset from 0 V by −75 mV, whereas for the annealed specimen the offset is +25 mV. The minimum of the dI/dV curve is offset from 0 V if the barrier is asymmetric. The magnitude of the offset is proportional to the magnitude of the asymmetry defined as the difference in barrier height at the top and bottom interfaces (Δφ). When the average barrier width and height from the Simmons model, together with the conductance minimum offset, are input into the Brinkman, Dynes, and Rowell model to calculate the value of the asymmetry, then Δφ is approximately 1 V for the as grown and 0.5 V for the annealed case.

To elucidate the origin of the asymmetry, APT analyses and conventional ex situ HREM were performed on specimens cut from pieces of the same wafers used for the in situ TEM studies. The HREM images (Fig. 3) clarify the contrast observed in the tunnel barriers of the in situ TEM images and allow the layer thicknesses to be determined. Analyses of APT reconstructions of as-grown specimens demonstrate that the intermediate contrast observed in the barrier region originates from a layer of CoFe oxide at the bottom FM/barrier interface that formed as a result of the leaking of O$_2$ into the deposition chamber for reactive sputtering of MgO from a Mg metal target. In essence, the MTJs were subject to an unintentional preoxidation step, which has been shown to
The barriers in both the as-grown and annealed specimens are asymmetric, but the magnitude of the asymmetry in the as-grown specimen is greater. This is because the layers in the as-grown sample are more compositionally distinct and sharply defined relative to the annealed specimen, and because the MgO barrier is in contact with CoFe on one side and by CoFe oxide on the other, which will have different work functions. The barrier region in the annealed specimen, by exhibiting more interdiffusion, is more symmetric. The barrier height has decreased slightly, which is consistent with a change from relatively pure MgO to MgO containing Co and Fe. The barrier width has increased, suggesting that some of the CoFe oxide layer may now be contributing to the tunnel barrier. The remaining small difference in barrier height between the top and bottom interfaces for the annealed specimens may be due to the thin region of CoFe oxide at the bottom FM interface that persists upon annealing.

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