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Mn diffusion and the thermal stability of tunneling spin polarization

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We examine the role of Mn diffusion in the thermal stability of tunneling spin polarization P by directly measuring P of Al/ AlO_x /Co/FeMn and Al/ AlO_x /Co₉₀Fe₁₀/FeMn junctions using superconducting tunneling spectroscopy (STS). We confirm Mn diffusion in our junctions using x-ray photoelectron spectroscopy after an ultrahigh vacuum 500 °C anneal. Surprisingly, and in contrast to the current belief, no drop in P is observed using STS. Therefore, though Mn diffuses significantly, it cannot be solely responsible for the drop in tunneling magnetoresistance observed after postdeposition anneals above 300 °C. © 2005 American Institute of Physics.

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Magnetic tunnel junctions (MTJs) demonstrate large room temperature tunneling magnetoresistance¹ (TMR) which makes them suitable for application in magnetoresistive random access memories (MRAMs).² A standard TMR stack generally consists of an antiferromagnet/ferromagnet/insulator/ferromagnet multilayer, where the antiferromagnetic (AF) layer is used to pin the direction of the magnetic moment of the adjacent ferromagnetic layer, and the ferromagnet-insulator-ferromagnet (F/I/F) sandwich is responsible for the TMR effect. The AF layer generally contains a Mn alloy (e.g., Fe₅₀Mn₅₀, Pt₅₀Mn₅₀) to allow device operation at elevated temperatures (above 150 °C).³ Presently, one of the major areas of research in MTJs is the miniaturization of these elements for application in MRAM and their integration with CMOS (complementary metal oxide semiconductor) processing.⁴ Successful integration of the MTJ in MRAM requires the device to be thermally resistant against standard high temperature CMOS processing steps (400–450 °C).⁵ However, postdeposition anneals of tunnel junctions below 300 °C enhances TMR, and those above 300 °C lead to its severe degradation.⁶ The physical mechanism behind this drop in TMR after anneals above 300 °C is not yet completely understood. Several causes have been suggested for this drop, among which Mn diffusion from the AF layer into the F electrode and towards the F/I interface is believed to play the principle role.^{6,7}

In this paper, we combine a study of the thermal stability of tunneling spin polarization (P) based on the superconducting tunneling spectroscopy (STS) technique⁸ with an x-ray photoelectron spectroscopy (XPS) analysis of Mn diffusion. The spin polarization of the tunneling electrons in the F/I/F junction is the fundamental parameter responsible for the TMR effect⁹ and is very sensitive to the interfacial density of states at the F/I/F interfaces.¹⁰ Any change in P should ensue from chemical and/or morphological changes at or near the F/I interface. We demonstrate that P in our Al/ AlO_x /Co/FeMn and Al/ AlO_x /Co₉₀Fe₁₀/FeMn junctions is ther-

mally stable up to 500 °C, even when Mn diffuses towards the I/F interface.

Detection of the influence of Mn diffusion in a conventional tunnel junction stack, for example, one consisting of FeMn/Co/ AlO_x /Co/Ta, is difficult to probe experimentally with XPS, since the escape depth of the photoelectrons is much less than the standard thickness of the top Co and Ta layers. Therefore, we deposited Al/ AlO_x /Co(200 Å)/FeMn(100 Å)/Co(200 Å) layers on silicon substrates using dc magnetron sputtering (base pressure <10⁻⁸ mbar), *in situ* annealed them at 500 °C in ultra high vacuum (UHV, pressure <10⁻⁸ mbar during anneal) for 30 min, and then studied them with *in situ* XPS (Al K_{α}). Logically, we assert that if Mn diffuses to the surface of the 200 Å thick top Co layer, it should also diffuse towards the AlO_x /Co interface below the FeMn layer. Also, any significant Mn accumulation near the surface of 200 Å thick top Co layer should be detectable by XPS. The AlO_x barrier layer (which is 10–22 Å thick) was formed by partially plasma oxidizing the 40 Å Al bottom electrode for 200 seconds.¹¹

Figure 1(a) shows the XPS spectra for Mn electrons measured before and after a 500 °C anneal. As expected, as-deposited samples show no evidence of Mn peaks in the intensity scan, confirming the absence of Mn at or near the surface of the 200 Å thick top Co layer. However, after the anneal, two explicit peaks appear near the energies of known Mn p -level peaks, which for pure Mn, are expected to be at 638.8 eV ($2p_{3/2}$) and 650.05 eV ($2p_{1/2}$), respectively.¹² This result is a proof of Mn diffusion from the FeMn layer towards the surface of the 200 Å thick top Co layer. Careful examination of the spectra show that the Mn peaks are shifted to higher binding energies, evincive of an oxidized state of Mn in the Co layer. In our sample, the $2p_{3/2}$ Mn oxide peak is found to be around 641.4 eV. The literature values for the $2p_{3/2}$ peaks of various manganese oxides are found to lie between 641–642 eV.^{12,13} The formation of Mn oxide near the surface of the top Co layer is purely due to the background partial pressure of oxygen in the chamber, which is introduced by the degassing of adsorbed oxygen from the sample plate during the anneal. Although we do not com-

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FIG. 1. (Color online) *In situ* XPS ($\text{Al } K_{\alpha}$) intensity spectra for (a) Mn peaks observed on the 200 Å top Co layer in the $\text{Al}/\text{AlO}_x/\text{Co}(200 \text{ Å})/\text{FeMn}(100 \text{ Å})/\text{Co}(200 \text{ Å})$ stack before and after *in situ* postdeposition UHV anneal at 500 °C. The dash-dotted (Mn) and solid (Mn_2O_3) lines indicate the expected $2p_{3/2}$ and $2p_{1/2}$ peak locations. (b) Co peaks for the same sample, the intensity of the Co $2p_{3/2}$ and $2p_{1/2}$ peaks decreases after the anneal.

pletely exclude the possibility of oxygen driven Mn diffusion (reported for a 30 Å thick CoFe layer by Ref. 14) towards the surface of the top Co layer, we strongly believe that our 200 Å thick top and bottom Co layers should inhibit such a process.

Figure 1(b) indicates the corresponding XPS spectra for Co $2p_{3/2}$ (778.1 eV) and $2p_{1/2}$ (793.0 eV) peaks. It can be seen that the spectral intensity of peaks for the as-deposited sample is much larger than when the sample has been annealed, confirming the decrease of Co near the surface of the layer. However, no oxidation of Co is evident, since there is no distinguishable shift in the peaks. Co $2p_{3/2}$ peaks are expected at 778.1 eV, and those for its oxides are expected between 779.8–780.2 eV.^{12,13} These results are in accordance with the fact that the (negative) free energy of formation is lowest for cobalt oxides, intermediate for manganese oxides, and highest for aluminum oxides,¹⁵ making it difficult for Co to oxidize in the presence of Al and Mn. Figure 2 shows the Mn to Co spectral intensity ratio in our XPS measurements as a function of anneal temperature. The ratio is calculated by removing the background in the measurements, fitting the peaks to expected Mn and Co peaks, and then deriving the area under the curve. It is notable that the Mn/Co ratio at or near the surface of the 200 Å top Co layer

FIG. 2. Mn/Co intensity ratio measured in our XPS spectra as a function of postdeposition anneal temperature.

FIG. 3. (Color online) Conductance of $\text{Al}/\text{AlO}_x/\text{Co}$ (a) and $\text{Al}/\text{AlO}_x/\text{Co}_{90}\text{Fe}_{10}$ junction (b) at 0.3 K in zero field and an applied field of several Tesla. The solid lines are theoretical fits.

starts increasing around 300 °C, which has been reported as the onset temperature for TMR collapse.⁶

To measure the effect of Mn diffusion on P , cross-stripped tunnel junctions with and without FeMn were prepared similar to the XPS samples. A 60 Å Ta capping layer was added on top. The junctions have an area of $400 \mu\text{m} \times 400 \mu\text{m}$ and a resistance-area product of roughly $10^5 \text{ k}\Omega \mu\text{m}^2$. Current-voltage ($I-V$), and conductance-voltage ($dI/dV-V$) characteristics are measured in a four-terminal configuration using a standard lock-in technique. Our Al bottom electrodes become superconducting at about 2.2 K (Ref. 8) and have critical fields of 4.5 T. Figure 3 shows representative measurements of an $\text{Al}/\text{AlO}_x/\text{Co}$ and an $\text{Al}/\text{AlO}_x/\text{Co}_{90}\text{Fe}_{10}$ junction at 0.3 K. In zero field the conductance reflects the superconducting density of states with its sharp peaks at the band-gap edge. In a magnetic field the conductance shows four maxima due to the Zeeman splitting of the density of states. The P is directly revealed by the asymmetry in the maxima⁸ and extracted by a fit of the model based on the Maki theory.^{16,17} This model accounts for the effect of orbital-depairing and spin-orbit scattering on the superconducting density of states.⁸ The extracted P ($38\% \pm 1\%$) for Co and ($48\% \pm 1\%$) $\text{Co}_{90}\text{Fe}_{10}$ junctions are in fair agreement with earlier work.¹⁸

Figure 4 shows P as a function of postdeposition anneal temperature for junctions which do (closed squares) and do not (open circles) contain an FeMn layer. Remarkably, P does not suffer any degradation in response to anneal up to 500 °C for both types of ferromagnets, independent of the presence of FeMn. Also, the absolute values of P for a particular ferromagnet does not change before and after the anneal, irrespective of Mn diffusion into the layers. This result is in qualitative agreement with the work of Kim and Moodera,¹⁹ who report that Mn concentrations as high as 30% in $\text{Al}/\text{AlO}_x/\text{Co}_y\text{Mn}_{1-y}$ junctions have only a weak negative effect on the P . In addition, the anneals do not affect other junction parameters such as junction resistance and the superconducting band gap of our Al electrode. The thermal robustness of P above 300 °C (evident in Fig. 4) is in sharp contrast with the effect of postdeposition annealing on the TMR of MTJs. In order to clarify this apparent contradiction further experiments are indispensable. The stable

FIG. 4. (Color online) P measured after an *in situ* 30 min postdeposition UHV anneal in $\text{Al}/\text{AlO}_x/\text{Co}$ and $\text{Al}/\text{AlO}_x/\text{Co}_{90}\text{Fe}_{10}$ junctions which do (closed squares) and do not (open circles) contain an FeMn layer. This data shows that P is not affected by the presence of an FeMn layer on top of the ferromagnet.

P in our junctions suggest that the TMR degradation may not be due to a degradation of the intrinsic P of the AlO_x/Co or $\text{AlO}_x/\text{Co}_{90}\text{Fe}_{10}$ system, but instead a result of extrinsic influences, such as the diffusion of impurity atoms into the barrier or to one of its interfaces. It is notable that our junctions are annealed in UHV (base pressure 10^{-9} mbar), as compared to earlier work by Cardoso *et al.* and Lee *et al.*^{6,14,20} who used vacuum chamber pressures around 10^{-6} mbar. We have already shown in junctions without FeMn, that UHV anneals preserve P as compared to similar junctions annealed in an Ar gas environment, that was known to possess a low concentration of gas impurities.²¹ Two other facts contributing to separate effects should be taken into consideration: (1) In our Al/I/F system, only the I/F interface can be studied. This I/F interface is much different from the F/I interface due to the crucial oxidation step used to form the Al oxide, and (2) the diffusion of Mn can alter the magnetic properties of the AF/F layers (see, for example, Refs. 6, 14, and 20).

We now turn our attention to another interesting observation. Typically, anneals below 300 °C enhances TMR. One explanation of this enhancement in TMR is an improvement of P due to migration of oxygen from the bottom F electrode into the AlO_x barrier.²² This stoichiometric redistribution of oxygen in the barrier results in a sharper interface and improved barrier properties. Consequently, the barrier height should increase, and spin-independent tunneling should decrease, both leading to higher TMR. Another explanation which concerns both electrodes is the possibility of a change in the ferromagnet structure at the interface after the anneal. However, our measurements do not show an increase in P when the Al/I/F stack is annealed at 100–300 °C,

which indicates that there is no change at the I/F interface or in the structure of the F electrode which contributes to enhancement of P , and subsequently, TMR. Therefore, the second explanation, i.e., change in the F electrode structure is not supported by our measurements.

In summary, we investigated Mn diffusion in Al/I/F junctions and its effect on the P of the electrons tunneling from the ferromagnet. Contrary to the current belief, we have shown that P in $\text{Al}/\text{AlO}_x/\text{Co}$ and $\text{Al}/\text{AlO}_x/\text{Co}_{90}\text{Fe}_{10}$ junctions is thermally stable up to 500 °C, despite the likelihood of Mn diffusion towards the I/F interface.

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