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A very important process step in the fabrication of magnetic tunnel junctions (MTJs) is the application of a modest anneal step in the presence of a high magnetic field. Roughly, a doubling of the magnetoresistance (MR) ratio is commonly observed. We show that both AlO_x as well as TaO_x MTJs with $Co_{90}Fe_{10}$ electrodes have similar oxidation time and anneal temperature dependencies of the MR ratios. In both cases, the maximum MR ratio shifts to higher oxidation times with annealing. TaO_x MTJs are, in this sense, good model systems. From photoconductance experiments we find that for TaO_x MTJs, this shift in maximum MR is accompanied by a similar shift of the zero crossing of the oxidation time dependent barrier asymmetry. This directly supports the point of view that for obtaining the highest MR ratio one should anneal MTJs that would be characterized as "slightly overoxidized" in the as-deposited state. We argue that this result can be understood by a homogenization of the oxygen distribution in the barrier, and/or a change of the *bottom* barrier-electrode interface. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1883324]

Ever since the discovery of large room-temperature magnetoresistance (MR) effects in magnetic tunnel junctions (MTJs),[1] improvement of the MR ratio has been one of the aims of the research of these structures. Higher MR ratios translate into increased signal to noise ratios in applications, such as magnetic random access memory (MRAMs).[2] Several groups have found that subjecting the commonly used AlO_x MTJs to a modest temperature treatment, up to roughly 200–300 °C for several tens of minutes, in the presence of a high magnetic field, significantly enhances the MR ratio.[3,4] Annealing at even higher temperatures is accompanied by a sharp drop in the MR ratio. The latter effect is probably related to the diffusion of impurities into the barrier layer,[5] but will not be discussed further in this letter.

The increase of the MR ratio has been attributed to a redistribution of the oxygen in the barrier layer,[3] and/or a change of the barrier interface structure.[6] However, obtaining *direct* evidence of changes in the barrier layer is difficult. Due to the interfacial sensitivity of the spin polarized tunneling process,[7] small changes can already have a profound influence on the MR effect. Also, due to the extremely small barrier thickness, the usefulness of techniques with only modest depth resolution, such as Rutherford backscattering spectrometry or x-ray photoelectron spectroscopy is rather limited.

Previously we have shown that, with the use of a photoconductance method, structural changes in the barrier as a function of oxidation time have a profound influence on the barrier height and asymmetry.[8,9] From these earlier studies, photoconductance seems therefore a suitable technique to *directly* study the influence of an anneal treatment in more detail.

In this letter, we use photoconductance to study the influence of an anneal treatment on the barrier potential shape of both AlO_x as well as TaO_x-based MTJs. AlO_x is the most widely used barrier material for applications,[2] while TaO_x offers the unique possibility to study directly the barrier asymmetry, by making use of interband excitations in this low band-gap material.[9] Upon annealing, both junction types show a significant increase in the MR ratio, consistent with earlier results,[3,4] as well as a shift of the "optimum" oxidation time to higher values. Our photoconductance results support the point of view that the increase of the MR ratio is caused by a modification of the oxygen distribution, and/or a change in the bottom electrode/barrier interface structure. We also show that for obtaining the highest MR ratio, one should anneal those junctions that would be characterized as "slightly overoxidized" in the as-deposited state.

The investigated samples are made by sputter deposition through metal contact masks on glass substrates, resulting in 60×60 and $200\times 200\ \mu m^2$ junction areas, for TaO_x- and AlO_x-based MTJs, respectively. The following layer stack is used: Glass//3.5 Ta/3.0 $Ni_{80}Fe_{20}$/10.0 $Ir_{20}Mn_{80}$/2.5 $Ni_{80}Fe_{20}$/1.5 $Co_{90}Fe_{10}$/TaO_x or AlO_x barrier/4.0 $Co_{90}Fe_{10}$/10.0 $Ni_{80}Fe_{20}$/3.5 Ta, with all thicknesses in nanometers. The TaO_x or AlO_x barrier layers are made by first depositing 1.0 nm Ta or 1.7 nm Al over the complete substrate, followed by plasma oxidation for 8–16 s and 50–400 s, respectively.

After fabrication, the samples are annealed in an oven, under an argon gas flow. During annealing, a high in-plane magnetic field of approximately 1000 kA/m is applied to keep the $Ir_{20}Mn_{80}$ exchange bias layer aligned. Each anneal step takes roughly 25 min, after which the (magneto)conductance is measured and a photoconductance study is carried out. All MR measurements are taken at 5 mV, and the photoconductance experiments are carried out by illuminating the MTJs with variable photon energies, while measuring the

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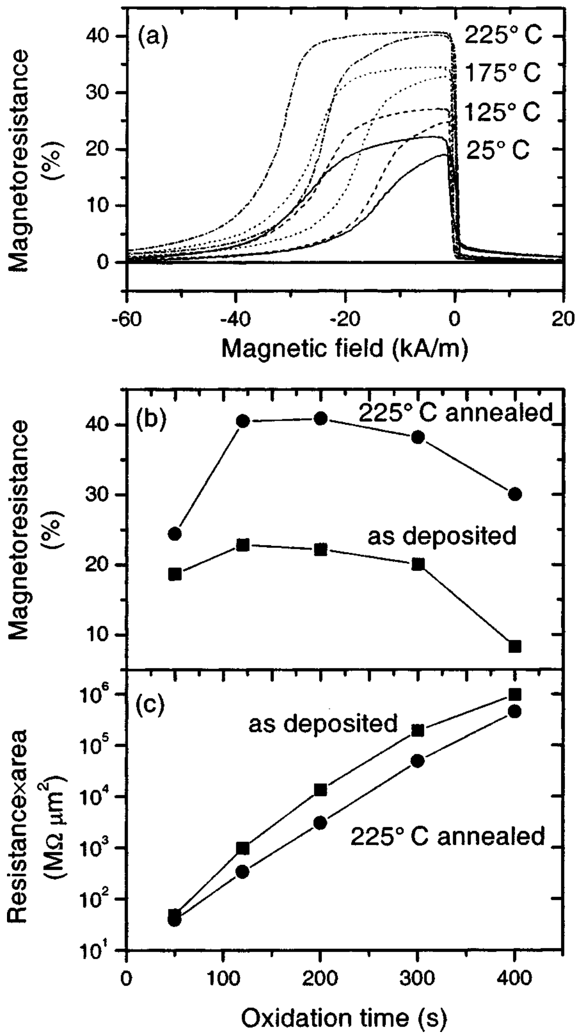

FIG. 1. MR ratio of AlO_x-based MTJs, as a function of (a) applied magnetic field, and (b) oxidation time for different anneal temperatures. In (a), the barrier was oxidized for 200 s, and in (c), the $R \times A$ product is shown for the studied junctions.

short-circuit photocurrent. Further details of the used measurement schemes can be found elsewhere.[8,9] Subsequently, the sample is subjected to a next anneal step, at a temperature that is 25 °C higher than during the previous anneal. To investigate the role of the oxygen distribution during annealing in more detail, the junctions are studied both as a function of anneal temperature as well as a function of the oxidation time. We will first focus on the results for AlO_x barriers, after which a comparison is made with results from the TaO_x MTJs.

In Fig. 1(a), MR curves of a typical AlO_x MTJ are shown, as a function of applied magnetic field, for different anneal temperatures. The barrier consists of a 1.7 nm Al layer, oxidized for 200 s. Besides an increase in the maximum MR ratio, also the shape of the curves changes. The applied field at which the pinned layer switches, shifts to higher negative fields, and the high resistance "plateau" becomes more flat. These effects are caused by the improvement of the exchange biasing during heating in a magnetic field.[10] However, this cannot be the sole reason for the improvement of the MR ratio. Comparing the curves for 175 °C and 225 °C, hardly any improvement in the antiparallel alignment is visible. Still, a ~20% increase in the MR ratio is present.

To investigate this additional increase in the MR ratio, junctions with different oxidation times are studied in more detail [see Fig. 1(b)]. Similar to previous results,[8] a maximum as a function of oxidation time is visible. After an anneal treatment to 225 °C, a modification of the curve is visible. If the improvement of the MR ratio would have a purely magnetic origin, the relative increase would be independent of the oxidation time. However, the relative increase in MR is much larger for overoxidized MTJs (e.g., 400 s) than for underoxidized ones (e.g., 50 s). Also, a shift of the maximum is just visible from ~120 s to ~200 s. It should be noted that the MTJs with different oxidation times are all annealed in the same run, and that, after each consecutive anneal step, the *same* junction is measured. The small difference in relative increase between 120 s and 200 s can thus be regarded as significant. The above clearly demonstrates an influence of the oxygen content on the improvement of the MR ratio.

From photoconductance studies on the AlO_x MTJs, a small reduction in the barrier height ϕ of ~0.1 eV has been determined after an anneal treatment up to 250 °C (not shown), as compared to the as-deposited state. Although only a small effect, this indicates that the potential landscape of the barrier is modified by the anneal treatment. At the same time, the resistance×area ($R \times A$) product decreases [Fig. 1(c)], indicative of a reduction in ϕ. More direct evidence of such a modification will be visible from photoconductance experiments on the TaO_x MTJs. However, we will first focus on the magnetoelectronic properties.

In Fig. 2(a), results from magnetoconductance measurements on TaO_x-based MTJs are shown. The MR curves as a function of applied magnetic field are similar to those presented in Fig. 1(a) for AlO_x MTJs, and are therefore not shown separately. Again, a maximum for a certain oxidation time is seen, related to the "optimal" oxidation of the Ta layer. Although difficult to see, this maximum shifts to slightly higher oxidation times after an anneal treatment (from 10 s in the as-deposited state to 12 s after annealing at 150 °C), similar to the AlO_x MTJs [see Fig. 1(b)]. TaO_x MTJs are, in this sense, good model systems. In contrast to AlO_x, the MR ratio of TaO_x MTJs already start to severely deteriorate after annealing above 150 °C (not shown). First indications of this effect are already visible for the highest oxidation times at 150 °C. Moreover, the $R \times A$ product *increases* after annealing [Fig. 2(b)]. These differences with AlO_x MTJs might be related to the 250% expansion of Ta during oxidation, as compared to only 25% for Al.[11]

For these *same* junctions, the barrier asymmetry $\Delta\phi$ has been determined from the bias voltage dependence of the photoconductance.[9] We note that $\Delta\phi=0$ corresponds to the simple picture of an "ideal" symmetric junction. The results are shown in Fig. 2(c). A clear shift of the barrier asymmetry after annealing is observed. The oxidation time where the barrier profile is symmetric lies now at a higher value, roughly corresponding to the maximum in the MR ratio after annealing at 150 °C. Extending our previous results,[9] we conclude that for the highest MR, and thus a (laterally averaged) symmetric barrier profile, one should anneal junctions that, before annealing, would be characterized as slightly overoxidized.

The difference in the improvement of the MR between under- and overoxidized junctions, together with the modification of the barrier potential, *directly* indicates that either

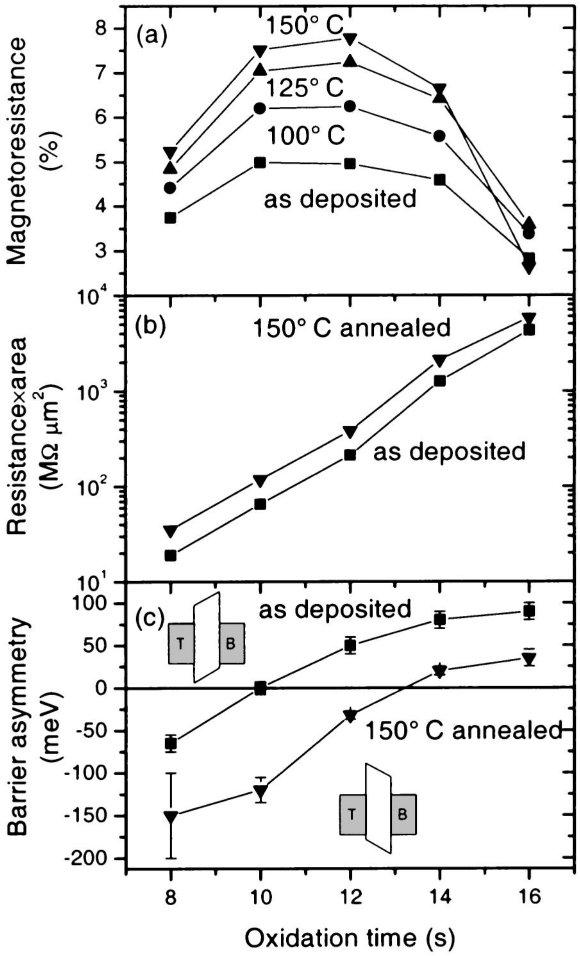

FIG. 2. (a) MR ratio, (b) $R\times A$ product, and (c) barrier asymmetry as a function of oxidation time for TaO_x-based MTJs, annealed at different temperatures. The barrier asymmetry in (c) is determined from the bias voltage dependence of the photoconductance (see Ref. 9). The insets in (c) represent energy diagrams defining the sign of the asymmetry relative to the top T and bottom B electrode.

the oxygen redistributes itself and/or the interface morphology changes with annealing. From direct measurements of the spin polarization in AlO_x-based superconducting junctions,[5] one can conclude that the top interface does not significantly change during an anneal treatment. This implies that the improvement of the MR, apart from the "trivial" exchange bias improvement, must originate from changes at the bottom interface, or from within the barrier layer itself. Due to the geometry of formation, the bottom interface will be less well defined than the top one.

As already shown by others,[12,13] the oxidation of barrier layers occurs predominantly along grain boundaries, implying that after oxidation a nonhomogeneous oxygen distribution is present in the barrier. For underoxidized junctions, not enough oxygen is present to completely oxidize the barrier layer. So, even when the oxygen redistributes itself after annealing, some regions of unoxidized barrier material are still left behind. The increase in the MR ratio is, in this case, mostly due to an improvement of the exchange biasing effect. For slightly overoxidized MTJs, the (small) pockets of unoxidized barrier material that are still left, are filled up during annealing by the oxygen that originally resided in small oxidized parts of the bottom electrode. Now an additional increase in the MR ratio is present due to a redistribution of the oxygen in the barrier, and/or an increase of the spin polarization of the bottom electrode due to a change in the interface morphology. Both effects can potentially lead to a change of the barrier potential shape, reflected in the change of $\Delta\phi$ and ϕ. These changes lead to a shift of the maximum MR ratio to higher oxidation times.

Summarizing, we have shown that the increase in MR ratio after an anneal treatment is accompanied by a modification of the barrier potential. We argue that this is caused by an oxygen redistribution within the barrier or at the *bottom* barrier-electrode interface. For obtaining the highest MR, one should anneal junctions that are characterized as slightly overoxidized in the as-deposited state.

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[1] J. S. Moodera, L. R. Kinder, and T. M. W. R. Meservey, Phys. Rev. Lett. **74**, 3273 (1995).
[2] S. Tehrani, J. M. Slaughter, M. Deherrera, B. N. Engel, N. D. Rizzo, J. Salter, M. Durlam, R. W. Dave, J. Janesky, B. Butcher, K. Smith, and G. Grynkewich, Proc. IEEE **91**, 703 (2003).
[3] R. C. Sousa, J. J. Sun, V. Soares, P. P. Freitas, A. Kling, M. F. da Silva, and J. C. Soares, Appl. Phys. Lett. **73**, 3288 (1998).
[4] S. S. P. Parkin, K. P. Roche, M. G. Samant, P. M. Rice, R. B. Beyers, R. E. Scheuerlein, E. J. O'Sullivan, S. L. Brown, J. Bucchigano, D. W. Abraham, Y. Lu, M. Rooks, P. L. Trouilloud, R. A. Wanner, and W. J. Gallaghar, J. Appl. Phys. **85**, 5828 (1999).
[5] C. H. Kant, J. T. Kohlhepp, H. J. M. Swagten, and W. J. M. de Jonge, Appl. Phys. Lett. **84**, 1141 (2004).
[6] K. I. Lee, J. H. Lee, W. Y. Lee, K. W. Rhie, J. G. Ha, C. S. Kim, and K. H. Shin, J. Magn. Magn. Mater. **239**, 120 (2002).
[7] P. LeClair, J. T. Kohlhepp, H. J. M. Swagten, and W. J. M. de Jonge, Phys. Rev. Lett. **86**, 1066 (2001).
[8] P. H. P. Koller, F. W. M. Vanhelmont, H. Boeve, R. Coehoorn, and W. J. M. de Jonge, J. Appl. Phys. **93**, 8549 (2003).
[9] P. H. P. Koller, H. J. M. Swagten, W. J. M. de Jonge, H. Boeve, and R. Coehoorn, Appl. Phys. Lett. **84**, 4929 (2004).
[10] J. van Driel, Ph.D. thesis, University of Amsterdam, Amsterdam, the Netherlands, (1999).
[11] P. Rottländer, M. Hehn, O. Lenoble, and A. Schuhl, Appl. Phys. Lett. **78**, 3274 (2001).
[12] A. E. T. Kuiper, M. F. Gillies, V. Kottler, G. 't Hooft, J. van Berkum, C. van der Marel, Y. Tamminga, and J. H. M. Snijders, J. Appl. Phys. **89**, 1965 (2001).
[13] P. Leclair, J. T. Kohlhepp, A. A. Smits, H. J. M. Swagten, B. Koopmans, and W. J. M. de Jonge, J. Appl. Phys. **87**, 6070 (2000).