Real-time evolution of tunneling magnetoresistance during annealing in CoFeB/MgO/CoFeB magnetic tunnel junctions

W. G. Wang,1,a) C. Ni,2 A. Rumaiz,1 Y. Wang,1 X. Fan,1 T. Moriyama,1 R. Cao,1 Q. Y. Wen,3 H. W. Zhang,3 and John Q. Xiao1,b
1Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716, USA
2Department of Materials Sciences, University of Delaware, Newark, Delaware 19716, USA
3State Key Laboratory of Electronic Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People’s Republic of China

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We report the study of the real-time evolution of tunneling magnetoresistance (TMR) in CoFeB/MgO/CoFeB junctions during annealing at 380 °C. The TMR quickly developed at the early stage of the annealing, with 200% magnetoresistance observed in less than 10 min, followed by a slow approach to saturation. This evolution of TMR was correlated with the structural changes, including crystallization of amorphous CoFeB electrodes and improvement of barrier quality during the annealing.


Since the first discovery of repeatable room temperature (RT) tunneling magnetoresistance (TMR),1 magnetic tunnel junctions (MTJs) have been extensively studied due to their wide applications in spintronic devices.2–5 The highest TMR value in conventional MTJs based on AlOx is around 70%,6 limited by the amorphous nature of AlOx barriers. In 2004, two groups independently reported giant TMR close to 200% in MTJs consisting of crystalline MgO barriers fabricated by reactive sputtering and molecular beam epitaxy, respectively. Later, 230% TMR was reported in MTJs employing amorphous CoFeB as electrodes and rf sputtered MgO as a barrier.9 So far, this method has been widely used because of its high reproducibility. The rf sputtered MgO layer has a strong (001) texture on the as-deposited amorphous CoFeB layer, and this (001) oriented MgO layer serves as a template for the (001) crystallization of CoFeB layers upon high temperature annealing at 350–500 °C, leading to a polycrystalline CoFeB/MgO/CoFeB sandwich with highly (001) out-of-plane texture. The grain-to-grain epitaxy in this structure satisfies the required band matching between the electrodes and the barrier,9 thus, the slow-decaying, half-metallic like $\Delta_1$ band gives rise to the giant TMR.1,12

Unlike in most AlOx based MTJs where annealing is used only as a post-treatment to improve the TMR,1,3,14 high temperature annealing above 350 °C is an indispensable step to achieve a high TMR value in the CoFeB/MgO/CoFeB based junctions.9,15–21 The optimal annealing condition should increase the crystallinity, thus maximizing the coherent tunneling in CoFeB/MgO/CoFeB sandwiches and minimizing other effects such as Mn diffusion induced at such high temperatures.16,21 The dependence of TMR on annealing temperature in these junctions has been studied extensively, with temperatures ranging from 250 to 500 °C.10,15–24 However, the annealing time, another equally important aspect as annealing temperature, seems to be ignored so far. In nearly all the reports of CoFeB/MgO/CoFeB based junctions with high TMR values, the annealing time was routinely used for 1–2 h.10,15–24 In this letter, we report the study of the real-time evolution of TMR during annealing at 380 °C by monitoring the TMR values in samples cooled to RT and maintained at 380 °C. Valuable information about the development of giant TMR in the CoFeB/MgO/CoFeB based junctions was obtained in this investigation. Another advantageous point of our study is that the annealing was done in air,25 which allowed accurate temperature control and fast turnover rate. We demonstrated that the TMR as high as 230% can be achieved by annealing in air with proper protective layers, without the need of high vacuum and high magnetic field during annealing.5,9,15,16,20,24,26

The samples were deposited in a magnetron sputter system with a base pressure of 5 × 10−8 Torr. The sample structure was Si/SiO2/Ta 7/Ru 20/Ta 7/CoFe 2/IrMn 15/CoFe 2/Ru 1.7/CoFeB 3/MgO 1.5–3/CoFeB 3/Ta 8/Ru 10, where the numbers are the layer thicknesses in nanometers. A thick Ru layer was used for the better performance at high annealing temperatures (Ref. 20). A combinational technique was used to form a wedge-shaped MgO barrier layer on the wafer. After the fabrication of blanket films, the MTJ samples with sizes from 5 to 100 μm were defined by photolithography and ion-beam milling. A 150 nm thick SiO2 layer was deposited as the insulation layer between the bottom and top electrodes. Finally, a Ti 15 nm/Au 150 nm bilayer was deposited as both the protective layer and contact electrode. The annealing was performed in air on a specially designed sample stage allowing simultaneous annealing of up to 410 °C and four-probe measurement of TMR.

First, we performed the annealing at 380 °C for different time durations and subsequently cooled the MTJs to RT under a magnetic field of 600 Oe for TMR measurement. The TMRs for the as-prepared MTJs were only 5%–8%, as shown in the inset of Fig. 1. Upon heating up to 190 °C for a few seconds and cooling down to RT in the field of 600 Oe, the exchange pinning was established and the MR reached about 25%. We refer to this as the “0 s” TMR curve, as seen in Fig. 1. The same sample was successively annealed for different time durations at 380 °C and the representative TMR curves at RT are shown in Fig. 1. The TMR increased to more than 135% after only 50 s and reached 200% for less than 10 min of annealing. Finally, the TMR slowly leveled off with a maximum value of 230% reached in 38 min. This maximum TMR value achieved by annealing in air is close to the maximum TMR value of 260% found in other samples fabricated under the same condition and annealed for 1 h.
under the vacuum of $10^{-6}$ Torr. The TMR as a function of the annealing time at 380 °C is plotted in Fig. 2(a). The free layer switching field, defined by half of the width of the minor TMR loop in Fig. 1, also exhibited similar dependence on the annealing time, as shown in the inset of Fig. 2(b). The switching field increased from 4 Oe to around 18 Oe after only a few minutes of annealing and then slowly leveled off. These results reveal that most structural changes leading to the high TMR values, happen at the first few minutes of annealing at 380 °C. The corresponding resistance during the annealing in the parallel ($R_P$) and antiparallel ($R_{AP}$) states are plotted in Fig. 2(b). Again, one can see the quick increase in $R_{AP}$ with the decrease in $R_P$ at the very beginning of the annealing. This is the direct consequence of the development of the coherent tunneling of the slow-decaying, half-metallic like $\Delta_1$ band as well as the fast-decaying $\Delta_2, 3\gamma$, and $\Delta_5$ bands in CoFeB(001)/MgO(001)/CoFeB(001) sandwiches through the change in crystal structures during annealing. It is worthwhile to note that some junctions on the same wafer experienced different annealing effects. For example, one MTJ reached a maximum TMR of 190% after annealing for 12 min as shown in the inset of Fig. 2(a). However, the TMR started decreasing with further annealing instead of leveling off. The origin of this discrepancy is still not clear at present. Nonetheless, these data suggest that under our current experiment condition, the optimal time for annealing at 380 °C is between 10 and 15 min to maximize the yield of high TMR junctions. It also indicates that normal annealing duration of 1–2 h could probably account for the low TMR values observed in some MgO based MTJs.

In the second type of experiment, we measured TMR at 380 °C during annealing. The exchange pinning was lost at such a high temperature and the TMR was under larger thermal fluctuation compared with the RT measurement. Nevertheless, the evolution of TMR with time was still very clear. Figure 3 shows the dependence of TMR and corresponding $R_{AP}$ and $R_P$ on the annealing time. Again, one could see that the TMR immediately increased from 16% to about 33% after 50 s, reached 43% after 185 s, then slowly approached saturation. The initial drop in resistance was due to the much higher transmission probability in the MTJs at 380 °C compared with that at RT. The quick saturation of TMR at 380 °C again strongly suggests that the majority part of TMR growth during annealing was achieved in the first few minutes. Along with the TMR measurement at RT as shown in Fig. 2(a), these data demonstrate that, instead of regular annealing of 1–2 h, annealing as short as 10 min is enough to achieve TMR value larger than 200%, and further annealing will only slowly increase the TMR. This information could be particularly useful when MgO based MTJs are implemented in the mass production of devices such as magnetic read heads or magnetic random access memories, where the minimization of manufacturing cycle time will have a direct economic value.

In order to confirm the observations in the transport measurements, we performed the x-ray diffraction experiment in a sample with the structure of Si/SiO$_2$/CoFeB/CoFeB/MgO/CoFeB MTJs measured at 380 °C. Inset shows the TMR curve of the as-prepared junctions.
where the change of reflectivity in the CoFeB tent with the grazing incidence x-ray scattering experiments, in the first few minutes of annealing. This finding is consistent with the crystallization of amorphous CoFeB. The evolution of FWHM and lattice constant during annealing unambiguously demonstrates that the most structural changes necessary to achieve high TMR values occurred at the first few minutes of annealing at 380 °C. As a result, 10 min of annealing at 380 °C gives rise to a TMR value larger than 200%. The reduced annealing time could help solve the problem of Mn diffusion and reduce the overall fabrication time of CoFeB/MgO/CoFeB junctions. In summary, we performed the annealing time dependence study on the transport and structural properties of CoFeB/MgO/CoFeB based junctions. It was found that most structural changes necessary to achieve high TMR values occurred at the first few minutes of annealing at 380 °C. As a result, 10 min of annealing at 380 °C gives rise to a TMR value larger than 200%. The reduced annealing time could help solve the problem of Mn diffusion and reduce the overall fabrication time of CoFeB/MgO/CoFeB junctions.

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FIG. 4. (Color online) (a) θ-2θ scans of the film after annealing for different periods of time at 380 °C. (b) The annealing time dependence of the FWHM of the MgO (002) diffraction peaks and the calculated lattice constant.

15 nm/MgO 15 nm/CoFeB 3.5 nm/Ta 5 nm. Fig. 4(a) shows the θ-2θ scans for the film in the as-prepared state as well as after annealing for different time duration. Upon annealing at 380 °C for a few minutes, the intensity of the peaks increased, associated with the decrease in the peak width. At the same time, a weak (002) diffraction peak of CoFe started to emerge at around 65° (not shown), indicating the crystallization of amorphous CoFeB layers. The evolution of the full width at half maximum (FWHM) of the MgO (002) diffraction peaks and the calculated lattice constant is shown in Fig. 4(b). The FWHM of the (002) peaks, a good representation of the crystallinity of the MgO barrier, rapidly dropped at the first few minutes of annealing and then slowly leveled off in prolonged annealing. The lattice constant essentially behaved in the same manner; it experienced a sharp decrease at the beginning of annealing and then gradually approached the bulk value of 0.4213 nm. These results agree very well with the TMR measurements. It is known that the first 1–1.6 nm of MgO deposited on CoFeB could be amorphous. Not only did this amorphous part of the MgO barrier layer develop (001) texture but also the overall crystallinity of MgO was improved through annealing, accompanied with the crystallization of amorphous CoFeB. The observed evolution of FWHM and lattice constant during annealing unambiguously demonstrates that the most structural changes in the CoFeB/MgO/CoFeB sandwiches occur in the first few minutes of annealing. This finding is consistent with the grazing incidence x-ray scattering experiments, where the change of reflectivity in the CoFeB/AlOx based junctions rapidly occurred at the beginning of heat treatment.