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Influence of Oxygen Monolayer at Fe/MgO Interface on Transport Properties in Fe/MgO/Fe(001) Magnetic Tunnel Junctions

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The barrier thickness dependence of the resistance-area product for Fe/MgO/Fe(001) and Fe/FeO/MgO/Fe(001) samples is presented in this work. Our measurements provide evidence of Δ_1 Bloch states filtering in the presence of an oxygen monolayer at the Fe/MgO interface, in agreement with theoretical predictions. For the transmission probability, the oxygen monolayer is shown to form an additional barrier equivalent to two MgO monolayers. Unexpectedly, the interfacial oxygen strongly reduces the conductance in the antiparallel configuration of magnetizations, and has only a small effect on the tunnel magnetoresistance. © 2012 The Japan Society of Applied Physics

In recent years, magnetic tunnel junctions (MTJs) have been of major interest for scientists and engineers because of their high potential for spintronic applications[1)] and for gaining an understanding of the basics of spin dependent tunneling.[2–4)] This interest has been strongly enhanced by predictions and observations of high tunneling magnetoresistance (TMR) values in single-crystal MTJs based on the MgO tunnel barrier.[5–10)]

According to Butler's theory,[5,6)] along the Δ direction where $k_{\parallel} = 0$, the transport properties of Fe/MgO/Fe(001) MTJs are governed by the electrons with Δ_i ($i = 1, 2, 2', 5$) Bloch state symmetries that decay differently within the barrier. For the parallel (P) configuration, the transport is governed by the Δ_1 states, which have the lowest decay rate into the barrier. For the antiparallel (AP) configuration, no minority Δ_1 states are available at the Fermi level so the conductance is dominated by Δ_5 states. This should lead to a huge TMR due to significant differences in the Δ_1 and Δ_5 decay rates. However, despite gradual improvements in the sample preparation, the TMR values of Fe/MgO/Fe(001) MTJs remain under 250% at 20 K and 180% at room temperature (RT), as reported by several groups.[10,11)] Experimental and theoretical efforts have been devoted to understanding the possible origin of limited TMR observations. Besides possible defects in the bulk crystallinity, the spin polarized tunneling is known to be highly sensitive to the interfaces. Any morphological or chemical deviation from the ideal Fe/MgO interfacial structure may strongly affect the transport. It has been suggested that a FeO layer at the Fe/MgO interface, even sub-stoichiometric, could strongly reduce the TMR.[12–15)] Although the presence of this interfacial FeO layer has been much debated, only a few experimental investigations of its influence on the transport exist.[16)] Here, we clarify the influence of the interfacial Fe–O bonding on the resistance-area (*RA*) product and the TMR of MTJs by comparing standard Fe/MgO/Fe(001) MTJs and oxygen-doped Fe/FeO/MgO/Fe(001) ones.

Systematic electrical measurements were carried out on sets of two samples differing only by their interfacial structures. Pairs of samples (A and B) were grown simultaneously by molecular beam epitaxy in the same ultrahigh vacuum (UHV) chamber, where A and B denote Fe/MgO/Fe and Fe/p(1 × 1)-O/MgO/Fe samples, respectively. The full stackings of samples A and B are MgO/MgO(7)/Fe(50)/MgO(1.1 to 2.3)/Fe(15)/Co(20)/Au(20) and MgO/MgO/Fe/p(1 × 1)-O/MgO/Fe/Co/Au, with thicknesses in nanometers. The FeO interfacial layer was obtained as follows. Before the deposition of the MgO barrier, sample A was stored in a UHV chamber adjacent to the growth chamber. Then, molecular oxygen was introduced through a leak valve and adsorbed at RT on the free Fe(001) surface of sample B. Since the adsorbed amount was controlled in real time by X-ray photoelectron spectroscopy (XPS), we could stop the deposition immediately after the adsorption of one oxygen monolayer. Subsequent annealing at 925 K (both samples were annealed) resulted in the p(1 × 1) ordering of the oxygen overlayer. The barrier and top layers were grown after cooling to RT. Importantly, the p(1 × 1)-O layer does not break the crystalline periodicity. Moreover, since the multilayers were deposited simultaneously, the thicknesses, and growth and annealing conditions for both Fe electrodes and the MgO barrier were strictly identical for samples A and B. Therefore, the differences in the transport characteristics we discuss below are only due to the presence of the additional oxygen monolayer. More details about the procedure and the characterization of the FeO interfacial layer can be found elsewhere.[16)]

We first investigated, by XPS, whether the growth of MgO has an influence on the oxygen layer. The XPS signals measured on the Fe/p(1 × 1)-O surface (open circles) and the Fe/MgO surfaces (open squares) are plotted on Fig. 1. Although the number of oxygen atoms in both layers is expected to be equal, the intensity for Fe/MgO (1 ML) (I_{MgO}) is higher than the one for Fe/p(1 × 1)-O (I_{FeO}). The possibility of having a sub-stoichiometric p(1 × 1)-O layer is ruled out by the results reported in ref. 16, in particular, the tunneling microscopy images. Also, the natural oxidation at the Fe/MgO interface is not the cause since the same excess of intensity is measured when MgO is deposited on the oxygen-saturated Fe/p(1 × 1)-O surface. Therefore, our results suggest that MgO contains an excess of oxygen, which agrees with both tunneling spectroscopy experiments[17)] and *ab initio* studies.[18)] The O 1s peak measured on Fe/p(1 × 1)-O/MgO (1 ML) is higher than the one measured on Fe/MgO (1 ML), which means that the p(1 × 1)-O layer is not consumed by the growing MgO. If MgO does not modify the p(1 × 1)-O layer, the O 1s signal on Fe/p(1 × 1)-O/MgO (1 ML) should be equal to $I_{FeO/MgO} =$

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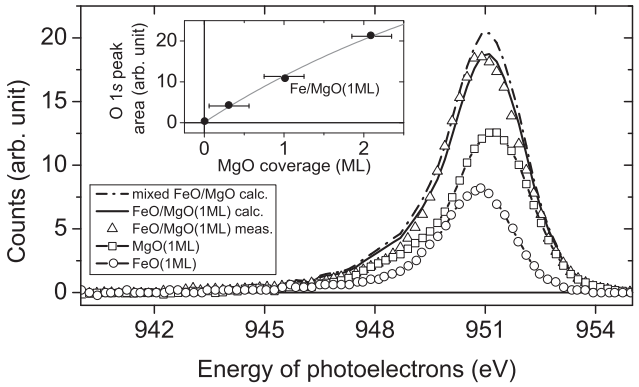

Fig. 1. O 1s peaks measured on Fe/p(1 × 1)-O, Fe/MgO (1 ML), and Fe/p(1 × 1)-O/MgO (1 ML) together with calculated spectra. A step function was removed from the spectra to account for the non resonant X-ray absorption. Inset: O 1s peak area measured by XPS on Fe/MgO surfaces and on Fe/p(1 × 1)-O. The line is an exponential fit to the data.

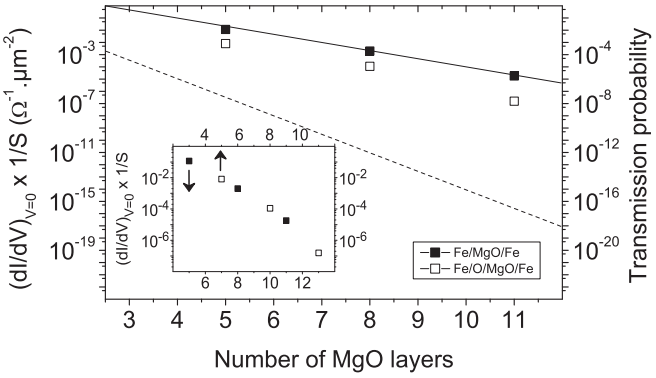

Fig. 2. Normalized conductance of A (filled squares) and B (open squares) samples for the P configuration. The continuous line (resp. dashed line) represents the transmission probability for the majority to majority (maj → maj) Δ_1 electrons (resp. Δ_5 electrons), and was extracted from refs. 5 and 6. The normalized conductance scale and transmission probability scale are proportional. In the inset, the results obtained for A (resp. B) samples are plotted according to the bottom scale (resp. the top scale). An offset of two MgO monolayers has been introduced between the two scales.

$I_{\mathrm{MgO}} + \exp(-1/\lambda\cos\alpha)I_{\mathrm{FeO}}$, where λ is the electron inelastic mean free path at the energy of the O 1s peak and α the angle between the detector and the surface normal. The electron escape depth $\lambda\cos\alpha = 4.24\,\mathrm{ML}$ has been extracted by fitting the intensities I_d of the O 1s peak obtained for a thickness d of MgO by $I_d = I_\infty[1 - \exp(-d/\lambda\cos\alpha)]$ (see inset of Fig. 1). Alternatively, the p(1 × 1)-O layer could be absorbed into MgO to fill hypothetical oxygen vacancies, or could segregate at the MgO surface. In this case, one would expect $I_{\text{mixed FeO/MgO}} \approx I_{\mathrm{MgO}} + I_{\mathrm{FeO}}$. The measured peak, plotted in Fig. 1, is in perfect agreement with the calculated $I_{\mathrm{FeO/MgO}}$, meaning that MgO does not disturb the Fe/p(1 × 1)-O surface.

Rectangular pillars were patterned in the top magnetic layer by a lift-off process, and ion beam etching stopped at the MgO barrier. The Fe/Co/Au pillars obtained were electrically connected by a full tungsten tip using an atomic force microscope (AFM). Further details can be found in ref. 19. The size of the connected dots varied from $100 \times 200\,\mathrm{nm}^2$ to $1 \times 3\,\mu\mathrm{m}^2$. The AP and P configurations were obtained by applying an external magnetic field. The *RA* product was deduced from the measurements using the following formula:

$$RA = \frac{A}{(dI_{\mathrm{P}}/dV)_{V=0}}, \tag{1}$$

where A is the surface area of the connected pillar, and I_{P} and V indicate the current for the P configuration and the applied bias, respectively. The TMR ratio is defined by

$$\mathrm{TMR} = \frac{(dI_{\mathrm{P}}/dV)_{V=0} - (dI_{\mathrm{AP}}/dV)_{V=0}}{(dI_{\mathrm{AP}}/dV)_{V=0}}. \tag{2}$$

According to theory,[5,6] the transmission probability for electrons with $k_\parallel = 0$ decays with barrier thickness d as $\exp(-2\kappa_{\Delta_i}d)$, where κ_{Δ_i} is the decay rate of the Bloch state for the Δ_i symmetry. The Bloch state with Δ_1 symmetry composed of s, p_z, and d_z^2 character decays slower than the state with Δ_5 symmetry containing $p_{x(y)}$, $d_{xz(yz)}$ character.

The situation becomes more complicated when the Bloch state symmetries start mixing, for example, when $k_\parallel \neq 0$. The Bloch states which do not have Δ_1 symmetry for $k_\parallel = 0$, start acquiring the s, p_z, d_z^2 character, resulting in the Δ_1-like decay rate within the thick barrier. Since overall conductance is defined as the interplay between the electrode states and the evanescent states in the barrier, it may happen that the appearance of even a small Δ_1 component in initially Δ_5 Bloch states may result in the κ_{Δ_1} decay rate. Based on these arguments, the dependence of the conductance as a function of the barrier thickness reveals the character of electronic states governing the transport.

In Fig. 2, we show the normalized conductance in the P configuration versus MgO thickness for A (filled squares) and B (open squares) samples. The continuous line (resp. dashed line) represents the transmission probability for the majority to majority (maj → maj) Δ_1 (resp. Δ_5) electrons, extracted from refs. 5 and 6. We observe that the conductance has a Δ_1-like decay rate of $0.37\,\mathrm{Å}^{-1}$, which is close to the theoretical value of $0.33\,\mathrm{Å}^{-1}$. This is direct evidence of a transport governed by the Δ_1 symmetry. The difference between the calculated decay parameter and the measured one can be explain in terms of diffuse scattering as explain in ref. 20. Furthermore, the presence of oxygen drastically reduces the conductance in the P configuration. In agreement with theoretical predictions,[12] the inset of Fig. 2 shows that the addition of one oxygen monolayer at the Fe/MgO interface attenuates the tunneling current, as does the addition of two MgO monolayers. Reference 12 provides an explanation for these observations. In Fe/MgO/Fe(001), the tunnel current flows mostly through the oxygen atoms of MgO ($\mathrm{O_{MgO}}$). In the presence of interfacial FeO, the Δ_1 states of Fe are involved in the interfacial Fe–O s,p bonds and their density shifts from the Fe atoms toward the oxygen ones ($\mathrm{O_{FeO}}$). However, the Δ_1 wave functions on $\mathrm{O_{FeO}}$ and on $\mathrm{O_{MgO}}$ are much different. The amounts of s and p components of the Δ_1 wave function are almost equal in $\mathrm{O_{MgO}}$ but differ by almost one order of magnitude in $\mathrm{O_{FeO}}$. As a consequence, only a small fraction of the wave function amplitude can be injected into the barrier because of this mismatch. Our data for the P configuration are in good

Table I. TMR values obtained for samples A and B (in %).

	MgO thickness		
	1.1 nm	1.7 nm	2.3 nm
Fe/MgO/Fe	50	117	142
Fe/O/MgO/Fe	38	50	115

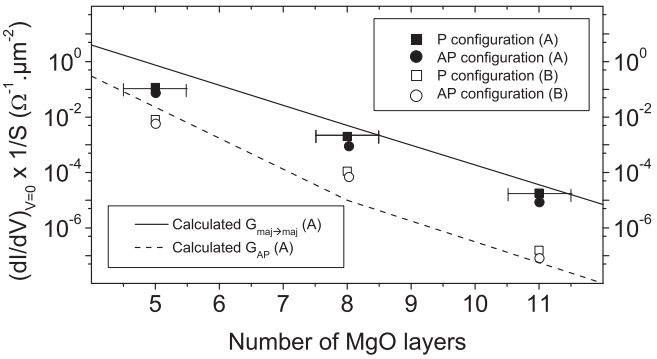

Fig. 3. Normalized conductance of samples A (Fe/MgO/Fe) and B (Fe/O/MgO/Fe) for the P and AP configurations, relative to the number of MgO layers. The continuous line represents the conductance calculated by Butler *et al.*[5,6] for the majority to majority channel.

quantitative agreement with theory. Nonetheless, we shall see below that an important discrepancy is observed for the AP configuration and the TMR.

Table I gives the TMR values for A and B samples for three different MgO thicknesses (5, 8, and 11 ML). As generally reported, the TMR values are far from the values of 10^3 orders predicted by the theories. In both samples A and B, the TMR increases as a function of the MgO thickness, which is the signature of Bloch states symmetry filtering by the barrier. Note that the TMR of 142% for Fe/MgO (2.3 nm)/Fe is lower than the usual 180%.[10,11] This is because the samples were not annealed after the growth of the top layers to prevent a change in the Fe/p(1 × 1)-O/MgO interface. With interfacial FeO, the TMR is reduced by a factor of less than 2.5. More than one order of magnitude was theoretically expected. The reason for this discrepancy is that in our measurements, the AP conductance is reduced by nearly the same amount as the P conductance (see Fig. 3), whereas, in theory, it was expected to be almost insensitive to the FeO.[12] Obviously, interfacial oxygen has a strong effect on the *RA*, but only a slight one on the TMR. Therefore, a hypothetical oxidation of Fe by MgO cannot account for the rather low TMR measured in Fe/MgO/Fe(001). Several experimental findings suggest that unexpectedly, a large part of the AP current in Fe/MgO/Fe(001) is carried by electrons with the Δ_1 component. First, the attenuation rate of AP conductance with the MgO thickness is close to the Δ_1 decay rate (Fig. 2 and ref. 10). Second, the AP conductance is much higher than the calculated one, whereas a good agreement is obtained in the P configuration. Third, the AP conductance is highly sensitive to the interfacial FeO, but the s,p Fe–O bonds mainly involve the same orbitals as the Δ_1 symmetry.

The origin of the Δ_1 behavior of G_{AP} remains unclear. It may be explained in terms of non-specular tunneling due to scattering at defects uniformly distributed in the barrier.[20,23] The interfaces may also play an important role in G_{AP}. Symmetry mixing could arise from symmetry break at the Fe/MgO interface.[24] The contribution of minority spin interfacial resonant states (IRS) is also suspected. These IRS are predicted to be close to the Fermi energy.[21,22] Experimentally, IRS have been found to participate to the transport with a Δ_1-like behavior, achieving the maximal contribution at 0.2 eV above the Fermi level.[19] Yet, a broad signature in the dI/dV characteristic has been observed that could extend towards the Fermi level. Further quantitative analysis of its width is needed to clarify its participation in the transport.

In conclusion, we performed systematic electrical measurements on sets of two MTJs with and without a p(1 × 1)-O monolayer at the Fe/MgO interface. In agreement with theory, the FeO layer reduces the conductance in the P configuration by one order of magnitude, equivalently to the addition of two MgO layers. However, in contrast to theory, the AP conductance is also strongly reduced. Consequently, the TMR does not greatly depend on the presence of interfacial oxygen. These results suggest that experimentally, Δ_1 symmetry plays a more important role in the AP conductance than so far thought. In complement, the present study shows that the presence of interfacial FeO can be inferred from the value of the *RA* product, but not from the TMR.

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