

Effects of the iron-oxide layer in Fe-FeO-MgO-Fe tunneling junctions

X.-G. Zhang,¹ W. H. Butler,^{1,2} and Amrit Bandyopadhyay²

¹*Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6114, USA*

²*University of Alabama, Tuscaloosa, Alabama 35487-0209, USA*

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First-principles calculations of the electronic structure and tunneling magnetoconductance of Fe-FeO-MgO-Fe tunneling junctions are compared to those of Fe-MgO-Fe. We find that an atomic layer of iron-oxide at the interface between Fe substrate and the MgO layer greatly reduces the tunneling magnetoconductance, due to the bonding of Fe with O which reduces the conductance when the moments in the two electrodes are aligned but has little effect when the moments are antiparallel. The TMR ratio (defined as the ratio of the change in resistance to the parallel resistance) decreases monotonically and exponentially with the increasing O concentration in the FeO layer.

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Spin-dependent tunneling junctions formed by trilayers of FM-insulator-FM where FM represents a ferromagnet have been shown to have relatively large magnetoresistance.¹⁻⁴ Much larger magnetoresistances have been predicted in recent calculations on epitaxial tunneling systems.⁵⁻⁸ The Fe-MgO-Fe tunneling junctions provide a good system for modeling because the Fe-MgO interface can form epitaxially and because coherent oxides can be grown that are only a few atomic layers thick. We have earlier⁶ calculated the electronic structure and the spin-dependent tunneling conductance of Fe-MgO-Fe sandwiches, using the first-principles layer-korringa-kohn-Rostoker⁵ (KKR) approach, and found that the majority spin channel conductance when the two Fe layers are aligned is dominated by contributions from $\mathbf{k}_{\parallel} = 0$. The minority channel and antiparallel conductances can be influenced greatly by interface resonance states especially for thin barrier layers. Similar calculations have recently been performed by Mathon.⁷ These earlier works predicted TMR ratios (defined as the ratio of the change in resistance to the parallel resistance) that are up to 6000% larger than experimentally measured ratios which are typically well under 100%.⁹ Meyerheim *et al.*^{10,11} presented evidence that an FeO layer often forms at the interface between the Fe and MgO when MgO is deposited onto an Fe(100) surface. This raises the question of whether the presence of the FeO layer may be the cause of the difference between the calculated TMR ratio and that observed in experiments and whether it is possible to greatly improve the TMR ratio by preventing the formation of FeO at the interface. It would also be desirable to understand the underlying mechanism of any reduction in TMR due to the FeO layer. In order to answer these questions, we report in this paper on first-principles calculations of the electronic structure and spin-dependent tunneling conductance of Fe-FeO-MgO-Fe tunneling junctions.

There are two different interfaces in the Fe-FeO-MgO-Fe stack. For the top interface between MgO and Fe, we use the same structure as in Ref. 6. The Fe layers are fixed at the experimental lattice constant for bulk Fe of 2.866 Å. The MgO lattice constant is taken to be a factor of $\sqrt{2}$ larger than that of Fe, therefore the (100) layers of the two materials can be matched epitaxially. We assume no vertical relaxations between the layers, and the Fe-O distance at the interface is

taken to be 2.16 Å. The bottom interface is assumed to contain a single atomic layer of FeO. The Fe atom of this layer sits at the bcc site of the substrate Fe lattice. There is experimental evidence¹¹ that the O sites are only about 60% occupied. The distance from the FeO layer to the first MgO layer was observed to be about 2.15 Å, and the intralayer Fe-O distance assuming a perfect lattice was 2.03 Å. The experimentally measured value¹¹ for the distance between the O in the FeO layer and the Fe atom underneath is 1.89 Å, but the error bar is large enough that the distance could be as large as 2.1 Å. There is also significant buckling in the FeO layer (about 0.2 Å).

The structure in our calculation is based on the experimental values, but with some modifications to take into account constraints needed to make the calculations feasible. Because of the partial occupation of the O sites, reflecting that the O atoms are too large to fit into the lattice, there is almost certainly some lattice disorder in the FeO layer. The Fe-O bond length tends to be longer in iron rich oxides (2.1 Å for FeO vs 1.9 Å for Fe₂O₃). Therefore it is reasonable to believe that the actual Fe-O bond length, both for interlayer and intralayer, should be longer than the nominal values obtained experimentally for an ordered lattice. Our calculation does not include the lattice disorder. Using the experimental values would place the Fe and O atoms too close together and possibly introduce large errors in the charge transfer between the atoms. Furthermore, the atomic sphere approximation (ASA) which we use in the calculation would not work well when the spheres representing the Fe potential and the O potential overlap too much. Based on these considerations, we chose the distance from the Fe-O layer to the first MgO layer measured from the O atom to be 2.18 Å, and the distance to the Fe substrate measured from the O atom to be 2.06 Å. The amount of buckling (vertical displacement between the Fe and the O atoms) in the FeO layer is chosen to be 0.4 Å which gives an intralayer Fe-O bond length of 2.07 Å. In order to fill the space with a minimal amount of overlap between the spheres, an empty sphere is inserted between the MgO and the Fe layers at the MgO-Fe interface. The self-consistent calculation is performed in the same manner as in Ref. 6. We assumed that all

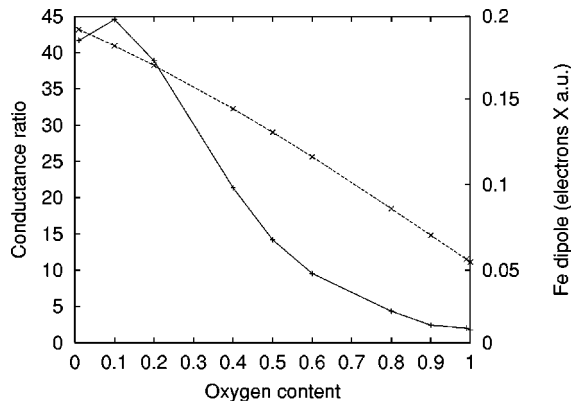


FIG. 1. Tunneling magnetoresistance as a function of O composition on the interface FeO layer. Solid line is conductance ratio, dashed line is dipole moment.

electron spins are collinear and that the magnetic order has the same periodicity as the two-dimensional lattice thus disallowing antiferromagnetic ordering within the same atomic layer. Antiferromagnetic coupling between layers is allowed. We used the coherent potential approximation¹² (CPA) for a substitutionally disordered O sublattice with two components, O and vacancy, to account for the underoccupancy of the O sites in the FeO layer. The composition of the O atom is varied from 0% for a completely pure Fe layer to 100% for a fully oxidized FeO layer.

Despite the large charge transfer between the Fe atom and the O atom within the FeO layer, the charge rearrangement necessary to correctly offset the bands of the MgO relative to those of Fe leads to very little charge transfer between layers, similar to the result we obtained for the Fe-MgO interface. We also find a significant moment of $0.19\mu_B$ (parallel to the Fe moment) on the O site of the FeO layer. This indicates very strong hybridization between this O atom and its neighboring Fe atoms. The strong hybridization of the Fe and O orbitals on the FeO layer, may be expected to affect the coupling of the electrons states from the Fe lead into the barrier and thus change the tunneling conductance.

The tunneling conductance is calculated using the same approach as in Ref. 6, which implements the Landauer-Büttiker conductance formalism^{13,14} within the first-principles layer-KKR framework. The tunneling conductances for the Fe-FeO_x-MgO-Fe stack were calculated for eight layers of MgO as a function of x between $x=0.1$ and $x=1$. The fractional O composition is modeled using the CPA (Ref. 12) which takes into account substitutional disorder between O atoms and vacancies, but does not allow structural disorder. The transmission probability calculated using the CPA captures the effects of disorder on the specularly transmitted (transverse momentum conserving) electrons, but neglects the contribution to the transmission from diffusely scattered electrons.¹⁵ For easier comparison, we also fixed the distance between the FeO layer and the first MgO layer for all O concentrations. This distance is somewhat larger than the interlayer distance between the Fe layer and the MgO layer used in Ref. 6. The results are plotted in Fig. 1 which shows that after initial small changes for low O concentration, the ratio of parallel and antiparallel conduc-

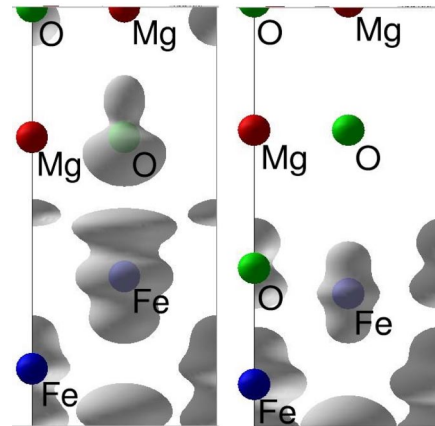


FIG. 2. The partial density of states at the Fermi energy due to the Δ_1 state in the majority spin channel near the interface region. Left panel, without the FeO layer; right panel, with the FeO layer.

tances drops exponentially as the O percentage increases above 50%. Thus any reduction in the O concentration of the interfacial Fe layer might be expected to have a large impact on the conductance ratio and the TMR.

In the same figure, we also plotted the change of the dipole moment on the Fe ASA sphere in the FeO layer as a function of O content. This moment drops from about 0.19 electrons \times Bohr (a.u.) at 0% O to 0.05 at 100% O. For reference, the corresponding Fe dipole moment on a clean Fe surface is about 0.22. The reduction in the dipole moment reflects the change of the electron density from one that is similar to a clean Fe surface at the Fe-MgO interface, where there is possibly little bonding between the Fe atom at the interface and any O atom in the MgO layer, to a density that lies almost entirely within the FeO layer, presumably in the form of Fe-O bonds, and very little density in the space between the Fe atom and the MgO layer when the FeO layer is completely oxidized. Because the Fe-O bonds involves mainly the sp electrons, and the d electrons are hardly affected by the presence of the O atoms in the layer, one can expect that the impact of the Fe-O bonds on the majority spin tunneling current will be much greater than the minority spin current, which is indeed the case we see in our calculations. This points to the formation of Fe-O bonds in the FeO layer as the main reason of the reduction of TMR.

What matters is the electronic structure at the Fermi energy. Since we have identified in earlier works^{6,16} that the dominant contribution of tunneling conductance is from the Δ_1 state of the majority spin channel, how this state couples to the MgO layer seems to be one of the critical factors affecting the TMR. For this we used the VASP code¹⁷ to calculate the partial electron density of states at the Fermi energy that corresponds to the Δ_1 state in the majority spin channel near the Fe-MgO interface, with and without the FeO interfacial layer. The results are shown in Fig. 2. It is clear that the introduction of the O atom to the top Fe layer greatly reduces the density of states in the interlayer region between this layer and the MgO layer. Reduction of the coupling of the Δ_1 state to the MgO layer would reduce the tunneling current of the majority spin channel and consequently the TMR.

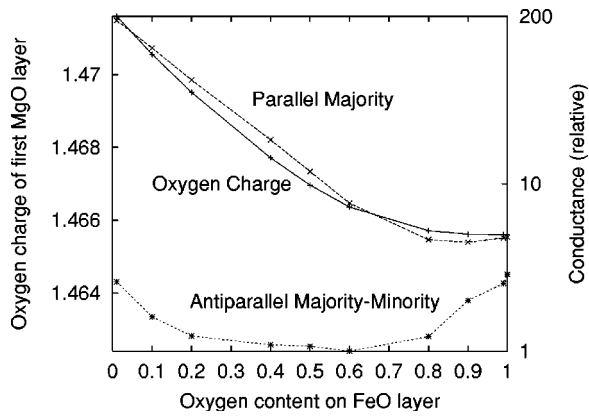


FIG. 3. Net charge on the O atom in the MgO layer next to the FeO (solid line) and the conductance of parallel majority and antiparallel majority-minority spin channels (dashed lines) as functions of the O concentration in the FeO layer. The conductances are normalized so that the minimum of the antiparallel majority-minority conductance is 1.

If there is a shift of electron density as described above, the shift should also be reflected by a change in the charge on the O site in the MgO layer next to the FeO interface in addition to the change in the conductance in each spin channel. We plotted in Fig. 3 the net charge on this O atom as a function of the O concentration in the FeO layer, along with the conductance of the majority spin channel for the parallel moment alignment, and the majority-minority channel for the antiparallel alignment. These two conductances dominate the contributions to the total conductance in their respective configurations. We see a striking correlation between the parallel conductance and the net charge on the O atom. This is strong evidence that the tunneling current is through the electron density between the Fe atom in the FeO layer and the O atom in the MgO layer next to the Fe. When the charge is moved away from this region to the Fe-O bond within the FeO layer, the tunneling current is reduced exponentially. On the other hand, the antiparallel tunneling current carried by mainly d electrons is hardly affected by this transfer of the charge. Noting that the charge within the O sphere in the middle layer of MgO is about 1.56, and that the variation of

the O charge on the first MgO layer is only about 0.03 and within 0.1 of that for the middle layer, we speculate that no Fe-O bond exists between the interface Fe atom and the O atom in the MgO layer. This is consistent with the well-known fact the Mg-O bonds are usually much stronger than Fe-O bonds. Thus, the absence of bonding between the interface Fe and the O in MgO layer, and the formation of the Fe-O bonds in the FeO layer is the key for explaining the dramatically reduced TMR.

Such a role of the FeO layer is further confirmed when we compare the tunneling density of states (TDOS) at $k_{\parallel}=0$, which is the electron density of states at each layer due to a single incident Bloch state from the left Fe lead, with and without the FeO layer. The change in the TMR is dominated by the change in the parallel majority spin conductance, which in turn is dominated by the contribution from $k_{\parallel}=0$. Comparing the TDOS in Fig. 4 for the Δ_1 state between the Fe-FeO-MgO-Fe stack and the Fe-MgO-Fe stack, we can see that the tunneling state decay rate is about the same within the MgO layer, and the coupling between the tunneling state in MgO and the outgoing Bloch state in the right Fe lead is also about the same. The big difference that causes more than one order of magnitude drop in the tunneling conductance comes from the reduced coupling of incident Bloch state from the left Fe lead through the FeO layer into MgO.

We also plotted in Fig. 4 the TDOS on individual atomic spheres. On layers where O atoms are present, they dominate the TDOS. Consequently, most of the tunneling current flows through the O sites. However, the symmetry of the wave function on the O site in the FeO layer is very different from that of the O site in the MgO layer. This is evident from the different ratios between the partial DOS in s and p components. The Δ_1 state in MgO has about the same order of magnitude s and p components on the O site, with the p component somewhat larger than s . On the O site of FeO, the p component is more than an order of magnitude larger than the s component. Thus in order for the wave functions to match across the layers, a much smaller fraction can be transmitted through the FeO layer compared to when there is no FeO present.

Now the picture is clear. Without the FeO layer, a sheet of electron density similar to that on a clean Fe surface exists

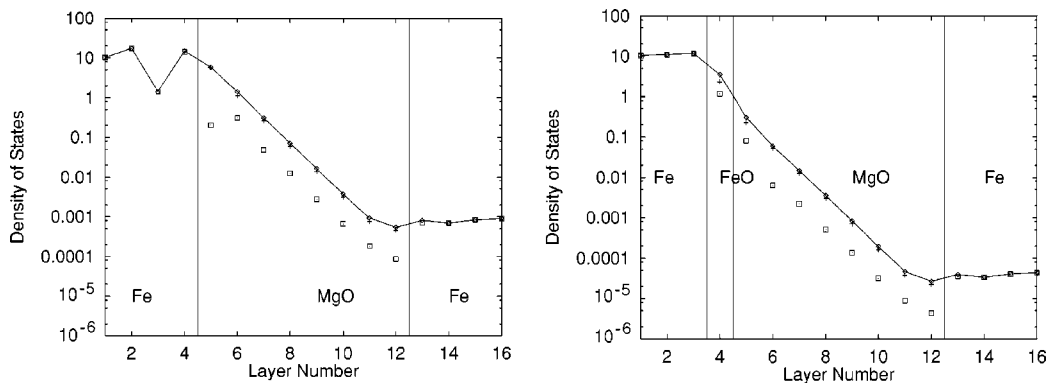


FIG. 4. Tunneling density of states for $k_{\parallel}=0$ for Fe(100)-8MgO-Fe(100) and Fe(100)-FeO-8MgO-Fe(100). Diamonds connected with lines are TDOS summed over each atomic layer. Crosses are contributions from the O spheres. Squares are from the Mg spheres in the MgO layer or from the Fe spheres in the Fe(100) layers or the FeO layer.

between the interface Fe atom and the first MgO layer and provides a path of low resistance for the tunneling current. With the FeO layer, as a function of increasing O concentration, the electron density becomes more and more concentrated within the FeO plane and confined within the Fe-O bond thus reducing the tunneling current through the Fe atoms. At 100% O the tunneling current flows almost entirely through the O atom. Due to the mismatch of the wave functions between the O orbitals within the FeO layer and those within MgO, the tunneling current for the parallel configuration is reduced while the antiparallel current is hardly affected, leading to a smaller TMR. Thus reducing Fe-O bonding, either by introducing different impurities or through other means, should be the most effective way of improving the TMR.

In the past, the tunneling process was often understood in terms of two inconsistent models, that of free electrons impinging on a square barrier and a model in which the tunneling conductance was proportional to the product of the densities of states on opposite sides of the barrier. First-principles calculations for epitaxial systems have demonstrated that tunneling is much more interesting and complicated than either of these models imply. We have previously emphasized the importance of the symmetry of the

Bloch states and of the complex energy bands in the barrier in determining the exponential decay with barrier thickness of the tunneling conductance.^{16,18} We and others have also emphasized the importance of interfacial resonance states in assisting transmission through the barrier.⁵⁻⁸ In this paper we emphasize a third phenomenon, the nature of the atomic bonding at the interface and its effect on the wave functions at the Fermi energy. A single atomic layer can change the conductance by more than an order of magnitude. Some of earlier calculations¹⁹ had hinted at the importance of the chemical bond effect based on the change in the magnetic moments of the interface layers when chemical bonds are formed. This work clearly demonstrates that the chemical bonding itself that has a direct impact on the conductance. Our result should apply to most tunneling experiments using Fe electrodes, since the formation of FeO layer is suspected to be a common phenomenon independent of the barrier material. At least one remaining part of the tunneling puzzle remains to be resolved, the effects of disorder within the barrier and at the interfaces.

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