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Atomic and electronic structure of the CoFeB/MgO interface from first principles

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First-principles calculations of the atomic and electronic structure of crystalline CoFeB/MgO/CoFeB magnetic tunnel junctions (MTJs) are performed to understand the effect of B on spin-dependent transport in these junctions. The authors find that it is energetically favorable for B atoms to reside at the crystalline CoFeB/MgO interface rather than remain in the bulk of the crystalline CoFeB electrode. The presence of B at the interfaces is detrimental to tunneling magnetoresistance (TMR) because it significantly suppresses the majority-channel conductance through states of Δ_1 symmetry. Preventing B segregation to the interfaces during annealing should result in an enhanced TMR in CoFeB/MgO/CoFeB MTJs. © 2006 American Institute of Physics. [DOI: 10.1063/1.2360189]

Magnetic tunnel junctions (MTJs) have recently aroused much interest because of their applications in random access memories and as magnetic sensors in disk drives. MTJs consist of a thin insulating layer separating two ferromagnetic electrodes. The electrical resistance of a MTJ depends on the relative magnetization orientation of the electrodes, which can be switched by an applied magnetic field. This phenomenon is called tunneling magnetoresistance (TMR) (for a review on MTJs and TMR see Ref. 1). Recently, large TMR values were predicted theoretically for MTJs based on (001)-crystalline MgO barrier layers epitaxially grown on (001) bcc Fe electrodes.^{2,3} This prediction was followed by experimental realizations of MTJs utilizing both epitaxial and textured Fe and Fe alloy electrodes,^{4,5} which showed that the resistance is enhanced by a factor of 3 at room temperature when the relative orientation of the magnetization of the electrodes changes from parallel to antiparallel. These achievements have triggered further interest in MTJs and the phenomenon of TMR.

For industrial production of MTJs, it is critical to be able to fabricate homogeneous MTJs on entire wafers such that the interface is flat on the lateral length scale of devices, about 100 nm, using a relatively cheap and fast sputtering process. It was found that amorphous CoFeB electrodes can be utilized to reduce interface roughness due to the absence of grains that are found in polycrystalline electrodes. Normally the CoFeB/MgO/CoFeB MTJs are prepared by sputtering deposition at room temperature, followed by annealing. Upon annealing, the amorphous CoFeB electrodes appear to crystallize near the interfaces in a bcc structure epitaxial to the MgO (001) surface. Several groups have observed a significant enhancement in TMR ratios after annealing.^{6,7} It is, therefore, evident that the crystallization of the electrodes plays an important role in this increase.⁸

It is not clear, however, what happens to the B distribution after annealing and what role it plays in spin-dependent transport. There are some indications that B mainly resides in the amorphous phase of CoFeB away from the crystalline CoFe produced by annealing near the interfaces,⁹ while there is some evidence of B having moved towards the CoFeB/MgO interface during annealing.¹⁰ This difference in experimental results may be due to film growth and/or insufficient resolution of the experimental techniques used to determine the B distribution.

Here we present results of first-principles calculations of crystalline CoFeB/MgO/CoFeB (001) to address both issues of B distribution and its effect on the spin-dependent tunneling across these MTJs. Total energy calculations reveal that it is energetically favorable for interstitial B atoms to reside at the CoFeB/MgO interface rather than remain in the bulk of the crystalline electrode. Due to the strong sensitivity of spin-dependent transport to the interface bonding and structure,¹¹ B has a profound effect on the tunneling spin polarization. We find that the presence of B at the interface is detrimental to TMR because it suppresses the conductance through the band of Δ_1 symmetry, which is known to be responsible for high TMR values in epitaxial CoFe/MgO/CoFe (001) MTJs.

Structural relaxations and total energy calculations are performed using the pseudopotential plane-wave method¹² implemented in the Vienna *Ab Initio* Simulation Package (VASP).¹³ The generalized gradient approximation¹⁴ is used for the exchange-correlation energy. We assume that the CoFe is in the form of an ordered alloy that has the CsCl structure. The interface has (001) texture with the MgO [110] direction parallel to the CoFe [100] direction so that transition metal atoms sit above the O atoms of the first MgO (001) layer (see Fig. 1). Both Fe and Co terminations are considered for the electrodes. Interstitial B atoms are assumed to occupy an octahedral site at the face center position of the conventional CsCl unit cell.

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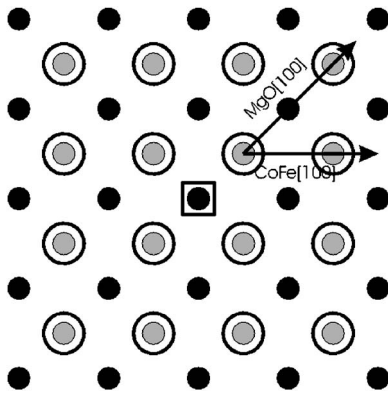


FIG. 1. Top view of the atomic structure at the CoFe/MgO (001) interface. The gray circles represent O atoms at the interface MgO layer and the black circles represent the Mg atoms. The larger unfilled circles represent the interfacial transition metal atomic layer (either Fe or Co) above the O atoms. The square indicates the interstitial position occupied by B in the transition metal atomic layer. The arrows indicate the orientation of the two materials.

In our calculations, we use the supercell which consists of 11 layers of CoFe and 5 layers of MgO. The in-plane lattice constant is constrained to be that of bulk CoFe, $a = 2.84 \text{ \AA}$. Due to the lattice mismatch of 5.2%, the MgO is compressed in plane and this induces a volume conserving tetragonal distortion of the barrier layer perpendicular to the plane of the film of about 4%. For the clean interface (no B) an equilibrium Fe–O distance of 2.23 \AA is found for the Fe terminated interface, while for the Co terminated interface the Co–O distance is 2.16 \AA . Ripples in the interfacial MgO (i.e., the displacement of O atoms relative to the Mg atoms in the same atomic layer) are less than 0.06 \AA for both terminations.

The total binding energy corresponding to the addition or removal of a B atom at a certain position relative to the CoFe/MgO interface is given by

$$E_{\text{tot}} = E(\text{clean CoFe}) + E(\text{free B atom}) - E(\text{fully relaxed CoFe} + \text{B}). \quad (1)$$

By $E(\text{structure})$ we mean the result of a total energy calculation for “structure.” Here “clean CoFe” refers to the supercell containing only the CoFe electrode, the MgO barrier, and no B; “free B atom” corresponds to a single B atom at the center of a large supercell, and “fully relaxed” refers to the CoFeB/MgO supercell. Positive binding energy means that the CoFeB/MgO relaxed supercell is stable with respect to dissociation into CoFe/MgO and a free B atom.

The total binding energy is calculated for two different B positions. In the first situation the B resides in the terminating transition metal layer at the CoFe/MgO interface (see Fig. 1). The second situation has one B atom in the “bulk” of the CoFe electrode five atomic layers away from the interface, either in an Fe layer or a Co layer. For both interface terminations the interface position has larger binding energy than either of the bulk positions. This suggests that in experimental systems B atoms should prefer to reside at the interface rather than in the *crystalline* bulk after annealing.

The total binding energy can be separated into two contributions. The first, which we will call the *chemical* binding energy E_c , is a positive contribution due to chemical bonding of the B atom to the host CoFe/MgO. The second, which we will call the *lattice distortion energy* E_d , is a negative contribution due to the structural distortion of the host lattice by

TABLE I. Total binding energy (in eV) and its two contributions for the interface and bulk positions of B.

	Fe layer		Co layer	
	Bulk	Interface	Bulk	Interface
E_{tot}	4.905	5.844	4.418	5.166
E_c	6.150	6.334	5.936	6.031
E_d	-1.245	-0.490	-1.518	-0.865

the interstitial. These two contributions can be extracted from the total binding energy in a straightforward fashion. The chemical contribution is given by

$$E_c = E(\text{relaxed CoFe}) + E(\text{free B atom}) - E(\text{fully relaxed CoFe} + \text{B}). \quad (2)$$

Here “relaxed CoFe” refers to a CoFe/MgO supercell disturbed in such a way that it has the same structure as if a B atom was present. The lattice distortion energy is simply the difference

$$E_d = E(\text{clean CoFe}) - E(\text{relaxed CoFe}). \quad (3)$$

We see from Table I that the interface position for B is energetically more favorable than the bulk position from both the chemical binding and lattice distortion contributions. However, the main contribution to the difference is from the lattice distortion. From this we conclude that the interface position is more favorable due to insufficient volume in the CoFe to accommodate an interstitial B atom. Here it is important to note that very similar binding energies are found in the absence of any MgO, i.e., for a bare CoFe (001) surface. This tells us that there is very little bonding of the B atom to the MgO when at the interface position. This is consistent with our finding that the MgO is disturbed very little with the inclusion of B atoms at the interface.

Next we study the effect of interfacial B on the bonding between MgO and CoFe. We do this by calculating the *work of separation* W_s for both clean and “boronized” interfaces. This is defined by

$$2W_s = E(\text{CoFe slab}) + E(\text{MgO slab}) - E(\text{CoFe/MgO}). \quad (4)$$

Here “slab” refers to the film surrounded by vacuum. No further atomic structure relaxations are performed in the calculation of the slabs (i.e., they are kept at the equilibrium structure found in the combined system). The factor of 2 in front of W_s accounts for the two interfaces in our supercell. The results are summarized in Table II.

For both the clean and boronized interfaces we find that the Co termination has larger work of separation by about 15%–20%. This implies that the Co termination is energetically more favorable than the Fe termination because of

TABLE II. Work of separation W_s (in eV per interface transition metal atom) for clean and “boronized” interfaces.

	Fe terminated	Co terminated
Clean	0.521	0.664
$\frac{1}{4}$ B coverage	0.372	0.437
Difference	-29%	-34%

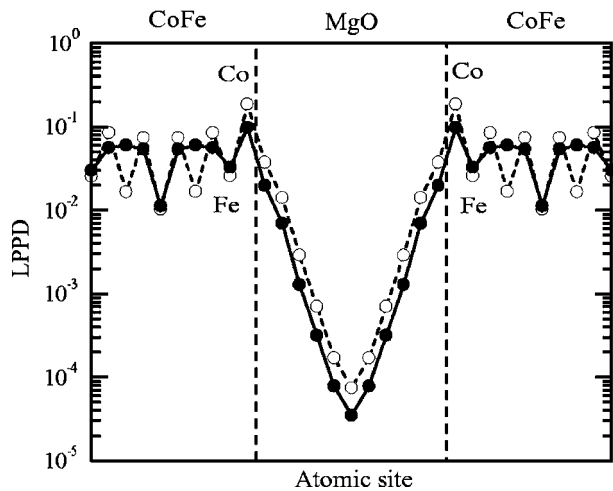


FIG. 2. LPPD (see text) for the majority state with Δ_1 symmetry at the Fermi energy for the Co terminated interface. The empty circles are for the clean interface and the filled circles are for the interface with $\frac{1}{4}$ B coverage.

stronger binding with the MgO film. We also see from Table II that the presence of B at the interface weakens the bonding between the CoFe and the MgO by about 30%.

Next we study the effect of interfacial B on the tunneling properties of the CoFe/MgO/CoFe junction. It is well known that the tunneling conductance in epitaxial CoFe/MgO/CoFe (001) MTJs is dominated by $k_{\parallel}=0$ states with Δ_1 symmetry due to their small decay parameter in MgO.¹⁵ Ono *et al.*¹⁶ have recently provided strong evidence that this is also the case for annealed CoFeB electrodes. Since the CoFe electrodes have only majority-spin states of Δ_1 symmetry near the Fermi level, impurities such as B primarily affect the parallel resistance and not the antiparallel resistance in a MTJ as pointed out by Zhang *et al.*¹⁷

We examine the layer projected probability density (LPPD) for the majority-spin state with Δ_1 symmetry at the Fermi energy with and without B at the interface. We consider only the $k_{\parallel}=0$ state for the supercell and neglect the possibility of any in-plane B disorder. In order to reveal the decay of the wave function into the MgO tunneling barrier we increase the thickness of the barrier from 5 atomic layers to 11, keeping the interface atomic structure consistent with the same minimum energy structure found with the smaller supercell. Figure 2 shows the results for both the clean Co terminated interface and the Co terminated interface with $\frac{1}{4}$ B coverage. The presence of B at the interface clearly reduces the interface LPPD with Δ_1 symmetry compared to the clean interface. This leads to a reduction in the amplitude of the evanescent Δ_1 state within MgO by a factor of about 2 (corresponding to a rigid shift downward in Fig. 2), thereby increasing the resistance of the MTJ by a factor of 2. Similar results were also obtained for the Fe terminated interface.

This increase in the interface resistance is consistent with the weakening of the bonding between CoFe and MgO due to the presence of B at the interface (see Table II). States with Δ_1 symmetry have s , p_z , and d_{z^2} characters (where z is the direction perpendicular to the plane of the interface) and contribute significantly to the Fe–O or Co–O bonding at the interface. When B is present at the interface this bonding (which, by symmetry, should have similar character) appears also to be weakened by the presence of more favorable Fe–B or Co–B in-plane bonding.

Zhang *et al.*¹⁷ found a similar reduction of the interface LPPD and interface bonding with the inclusion of excess interstitial oxygen atoms in Fe/MgO/Fe MTJs. Our calculations predict that the decay parameter of the Δ_1 state does not change with the inclusion of B at the interface, as is evident from the same slope of the two curves inside MgO in Fig. 2. This is due to the fact that the decay parameter is determined by the complex band structure of MgO and is independent of the electrodes except for the Fermi energy, which does not appear to change significantly with the inclusion of B.

Since the Δ_1 state does not contribute to the conductance of a MTJ when the two electrodes have antiparallel magnetizations, the increase in the resistance for the parallel configuration due to the presence of B atoms at the interface, discussed above, reduces the TMR. Since there is some evidence¹⁰ of B migration to the interface upon annealing, preventing B segregation to the interface should result in an enhanced TMR in CoFeB/MgO/CoFeB MTJs.

In conclusion, using first-principles total energy calculations we have shown that in crystalline CoFeB/MgO/CoFeB (001) MTJs it is energetically favorable for B to reside at the CoFeB/MgO interface rather than remain in the bulk of the crystalline CoFeB electrode. The presence of B at the interface reduces the TMR due to the suppression of the conductance through the Δ_1 band. Thus, preventing the presence of B at the interface should enhance the TMR in these junctions.

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