1 SCIENTIFIC HIGHLIGHT OF THE MONTH

First-principles modelling of magnetic tunnel junctions

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Introduction

Magnetic tunnel junctions (MTJ) are promising candidates for applications in spintronic devices such as magnetic random access memories, read heads and sensors [1]. The MTJs consist of two ferromagnetic layers separated by an insulating barrier layer. The physical quantity measured for signal detection is the tunnelling magnetoresistance (TMR), i.e. the relative difference in the resistance between parallel and antiparallel magnetizations of the electrodes. It was found that the TMR could be as high as 30% at room temperature in tunnel junctions based on ferromagnetic 3d-metal electrodes when alumina is used as the barrier layer (for a recent review, see [2]).

The magnitude of the TMR is determined by the spin polarization (SP) of the tunnelling current, which can be measured in experiments on superconductors [3]. It was generally accepted that the SP of the tunnelling current is an intrinsic property of the ferromagnets and is determined by the SP of the electronic density of states (DOS) at the Fermi energy [4]. Experimental results show, however, that the SP of the tunnelling current is strongly dependent on the structural quality of the tunnel junctions. Improvements in the quality of the alumina barrier and the metal/alumina interfaces result in an enhancement of the measured values of the SP. Experiments also show that the SP is dependent on the choice of the tunnelling barrier. Negative values of the SP were obtained at low applied voltage when tunnelling occurs from Co across a $SrTiO_3$ barrier [5], whereas it is positive across an alumina insulating layer [3]. We see, therefore, that the SP is *not* an intrinsic property of the ferromagnet alone but depends on the structural and electronic properties of the entire junction including the insulator and the ferromagnet/insulator interface. Thus, the realistic description of the magnetic tunnel junctions becomes increasingly important for a quantitative description of the SDT and for an accurate prediction of the TMR. This is a very complicated problem especially due to the *amorphous* structure of the alumina barrier layer and the lack of direct atomistic information about the structure and bonding at the ferromagnet/alumina interface. This is quite different from the situation with other metal/alumina interfaces so far studied in which the metal is grown on top of *crystalline* Al_2O_3

(see, for example, [6], [7, 8]).

As a first step in understanding the properties of Co/Al$_2$O$_3$/Co tunnel junctions we want to address two principal issues: 1) the atomic structure of the MTJ, and 2) the electronic structure of the MTJ. We have considered both Al- and O-terminated interfaces in coherent geometries which provide the *smallest* possible lattice mismatch between bulk fcc cobalt and crystalline α-alumina and have performed full geometry optimization of the structure by self-consistent spin-polarized calculations within density functional theory and the generalized gradient approximation using the total energy plane-wave pseudopotential code CASTEP [9]. The spin-polarized electronic structure of the Co/Al$_2$O$_3$ interfaces was studied by means of the scalar-relativistic linear muffin-tin orbital (LMTO) method [10]. Electronic properties of the Co/Al$_2$O$_3$/Co MTJ are discussed with the focus to understand mechanisms responsible for spin-dependent tunneling.

Atomic structure

We have constructed a realistic model for the atomic structure of the cobalt/alumina/ cobalt tunnel junction within a supercell approach by incorporating most of the important features of the real Co/Al$_2$O$_3$ thin-film system. The MTJs are produced by depositing a few tens of monolayers of aluminium film on top of the crystalline ferromagnet layer followed by thermal- or plasma- assisted oxidation to create the alumina tunnelling barrier (see e.g. [11]). The TEM images show that the alumina layer is grown on top of the (111) plane of fcc cobalt which exhibits large, predominantly [111] oriented grains [12]. Therefore, it is reasonable to assume that the cobalt film (deposited at the beginning of the manufacturing cycle) serves as a base with the bulk lattice parameter fixed in the plane parallel to the interface. The alumina is then formed by adjusting its structure to that of cobalt during the course of oxidation.

The amorphous state of alumina can not be directly modeled at present by first-principles methods due to the large number of atoms needed in the simulation cell. Therefore, we consider crystalline α-Al$_2$O$_3$ with the [0001] orientation on top of fcc (111) Co, as a first step in modelling a realistic Co/Al$_2$O$_3$/Co MTJ. We have carefully studied all the possibilities of relative crystallographic alignments of cobalt and alumina and identified the crystal structure with the minimal lattice mismatch. The lateral dimensions of our supercell correspond to a 2x2 surface unit cell of the (111) plane of fcc cobalt with the theoretical lattice parameter $a = 5.057$ Å. The experimental lattice parameter a of corundum is 4.759 Å which results in a 6% lattice mismatch. Two limiting cases of oxygen-rich and aluminium-rich interfaces were modeled in order to get a feeling of the influence of oxidation on the SDT device characteristics. For both the O- and Al-terminated interfaces we use a seven-layer-thick cobalt slab with four cobalt atoms per layer (28 cobalt atoms in total) and a seven-layer-thick alumina slab, the composition of the latter being dependent on the termination.

Spin-polarized plane-wave pseudopotential calculations of the MTJ in supercell geometry were made within the generalized gradient approximation with the code CASTEP [9]. In order to determine the relaxed structure of the MTJ, it was critical to perform an optimization of all the internal coordinates of the atoms as well as the height of the unit cell. The constraints of fixed lateral cell dimensions and frozen three middle layers of cobalt were imposed in order to

simulate the experimental conditions of the growth on the cobalt base. For a given cell size the atomic internal degrees of freedom were relaxed to give the minimum energy structure. The cell size was then varied and the relaxed structure was deduced from the minimum of the resultant binding energy curve. The relaxed structures are shown in Fig. 1.

We see from Fig. 1 that at the O-terminated interface the three oxygen atoms in the O{1} layer participate in bonding with the four cobalt atoms in the Co{3} layer. Since the O-terminated interface possesses P-3 symmetry all three oxygen atoms are equivalent so we label them O. Looking at the cobalt side, the four cobalt atoms are divided into the three equivalent atoms Co2 and the single atom Co1 which is centered on the axis of symmetry. This Co1 atom forms three equivalent bonds with surrounding O atoms with a bond length R(Co1-O)= 2.12 Å, whereas each of the other three Co2 atoms forms a bond with a single oxygen with a bond length R(Co2-O)= 1.97 Å. This difference in bond number between the Co sites causes the O-terminated interface to ripple by 10%. From the Al_2O_3 side of the interface, every oxygen atom has two inequivalent bonds R(Co1-O) and R(Co2-O) with the Co1 and Co2 atoms plus two inequivalent bonds with the aluminium atoms Al1 and Al2 in the layer Al{1} (R(Al1-O)= 1.84 Å and R(Al2-O)= 1.95 Å). In both interface terminations Al1 labels the aluminium atom within the first alumina layer Al{1} that is closest to cobalt, whereas Al2 labels the aluminium atom within the same Al{1} layer, but shifted along the z-direction towards the alumina side. The average Co-O bond length of 2.04 Å is within 5% of that in bulk CoO [13].

Fig. 1. The relaxed structure of the (a) O-terminated and (b) Al-terminated MTJs. The left-hand panel is a side view of the supercell, the right-hand panel is a layer-by-layer projection of the structure onto the (0001) plane using the Co{3} layer as reference. The layers are labeled by the chemical symbol of the element comprising the layer and are numbered from the bottom to the top.

At the Al-terminated interface two aluminium atoms in the Al{1} layer interact with the four cobalt atoms in the Co{3} layer as shown in Fig. 1. Atom Al1 occupies the fcc hollow site in the next layer, and the Al2 atom is at the hcp hollow site (these positions are identified

as hcp or fcc with respect to in-plane coordinate stacking). The Co1 atom does not have any bonds with the interfacial Al{1} layer, and each of the three equivalent Co2 atoms is bonded to one Al1 atom with a bond length 2.40 Å and to one Al2 atom with a bond length 2.58 Å. From the alumina side of the interface one Al1 atom is bonded to three Co2 atoms and the Al2 atom also has three Co2 nearest neighbours. The P123 symmetry of the cell includes a 3-fold rotation in addition to reflection. All the three Al-Co bonds originating from a particular Al atom are identical, the Co2-Al2 bond lengths being the longest. Interestingly, the average value of the Co-Al bond lengths, namely 2.49 Å, is equal to the average Al-Co bond lengths in CoAl intermetallic compound [14].

Electronic structure

The resulting spin- and layer-dependent DOS for the O-terminated interface are shown in the left hand panel of Fig. 2. The top two panels (a) and (b) display the LDOS of the O{2} and Al{2} layers in the middle of the oxide. We found that these LDOS are very similar to those obtained for the bulk α-Al_2O_3 [15], [16]. In the bulk α-Al_2O_3 the valence and the conduction bands are separated by a band gap which is, according to our results, equal to 6.2 eV at the Γ-point. Although this value is less than the experimental band gap of 8.8 eV [17] as a result of using the local density approximation (LDA), it is in good agreement with an all-electron full-potential LDA calculation [18]. In the presence of the interface with the Co metal the LDOS within the band gap of alumina (layers O{2} and Al{2}) is not exactly zero showing the presence of electronic states of the Co metal that propagate into the insulator barrier, decaying exponentially with the distance in the oxide layer. These metal-induced states are spin-polarized and are responsible for the spin-dependent tunnelling [3]. The Fermi level lies within the band gap of Al_2O_3 at about 3.5 eV above the top of the valence band.

The DOS of the inner Co{0} layer (panel (f)) is similar to the bulk DOS of fcc Co [19]. Although the major features of the DOS of the interfacial Co{3} layer bear close resemblance to that of the bulk Co{0} layer, the observe some differences as a result of the reduced symmetry of the interface as compared to the bulk and the covalent bonding between this Co{3} layer and the adjacent oxygen O{1} layer of Al_2O_3. In particular, the d band of the interfacial Co{3} layer is smeared out compared to the bulk (compare (e) and (f)), and the electronic states extend down to -10 eV as a result of the bonding with oxygen. This bonding does not, however, quench the interface magnetism, the magnetic moment of the interfacial Co{3} layer being 1.68 μ_B. This is different from what was found for the Co/HfO_2(001) interface [20], where the majority d band of the interfacial Co layer was not completely occupied and consequently the magnetic moment of this layer was strongly reduced compared to the bulk.

The DOS of the oxygen O{1} layer at the interface is very different from that in the 'bulk' of alumina O{2} layer (compare (d) and (a)) due to the covalent bonding between the $2p$ orbitals of oxygen and the $3d$ orbitals of cobalt. The pronounced four peaks in the energy interval between -3 eV and -8 eV for both the majority- and minority-spin electrons are associated with the formation of the bonding states. In addition to the bonding levels below the d bands, the oxygen DOS displays a broad band of antibonding states that extends up to about 2 eV above the Fermi

energy. The exchange splitting of the d bands of Co and the bonding between the d orbitals of Co and the p orbitals of O induce a splitting of these antibonding states. Contrary to the bonding states, this splitting is large, mirroring the exchange splitting of the surface Co d states. The antibonding states are almost fully occupied for the majority spins and are partly occupied for the minority spins. This leads to an induced magnetic moment of 0.07 μ_B on the oxygen sites. The LDOS at the Fermi energy is larger for the minority-spin electrons as compared to the minority-spin electrons, i.e. the spin polarization in the density of states at the Fermi energy is negative. The DOS of the Al{1} layer adjacent to the interfacial O{1} layer does not differ significantly from the DOS of the Al{2} layer in the bulk of alumina (compare panels (c) and (a)). Although a trace of the antibonding Co-O states is still visible at the energies within the band gap, the bonding between the Al and O dominates in the LDOS formation within this layer.

Fig. 2. Layer-projected spin-dependent densities of states of the O-terminated $Co/Al_2O_3/Co$ MTJ (left hand panel) and Al-terminated $Co/Al_2O_3/Co$ MTJ (right hand panel) as a function of electron energy. The majority- and minority-spin densities of states are shown by arrows pointed up and down respectively. The Fermi level is denoted by the vertical line.

The electronic and magnetic properties of the Al-terminated interface differ from those of the O-terminated one. The main difference comes from the fact metallic character of the metal/oxide interaction (see below) results in the sizeable LDOS of the interfacial Al{1} layer at the Fermi

energy which is typical for metals (see the right hand panel (d) in Fig. 2). The DOS of the oxygen and aluminium layers within the interior alumina are qualitatively similar to those obtained for the O-terminated interface (compare panels (a) and (b) in Fig. 2). There is, however, a difference in the position of the Fermi energy: in the case of the Al-terminated interface it is shifted towards the bottom of the conduction band. As can be seen from panel (d), the SP of the LDOS at the Fermi level on the interfacial Al{1} layer is slightly negative.

Character of bonding at the interfaces in $Co/Al_2O_3/Co$ MTJ

The electronic structure results indicate strong covalent bonding at the interface between Co{3} layer and the adjacent oxygen O{1} layer of Al_2O_3 in O-terminated MTJ. Fig. 3a shows charge-density contours of the Co/Al_2O_3 system in the (100) Miller plane of the supercell. The O atom at the interface shares the charge with the two interfacial Co1 and Co2 atoms. This partial localization of the electron density in the region between the atoms is an additional evidence of the covalent character of the Co-O bonding. The strongest covalent bonding is between the Co2 and O atoms which have the smallest bond length of 1.97 Å. The Co1 atom at the interface has much weaker bonding with O. There is little electron charge propagating from the O atom to the nearest Al1 atom and the region between them is characterized by a very low charge density. This fact and the sizeable charge transfer between the Al and O demonstrate the dominance of the ionic character in the Al-O bond, which is known from previous studies of bulk alumina [17].

Fig.3. Charge density contours (in atomic units) of the (a) O-terminated and (b) Al-terminated $Co/Al_2O_3/Co$ MTJ.

The Al-terminated interface is characterized by metallic character of bonding as it was evidenced from resulting electronic structure. The interfacial Al{1} layer can be considered as a termination of a metal substrate comprising the Co metal layer and the Al monolayer and the LDOS of the interfacial Al{1} layer is sizeable at the Fermi energy which is typical for metals. Fig. 3b shows the charge-density map of the Al-terminated Co/Al_2O_3 system in the (110) Miller plane of the supercell. As is seen from the Fig. 3b, the value of the charge density at the interface is

comparable with that in the interstitial region of bulk Co, which indicates the metallic character of the bonding between Co and Al at the interface.

As is known from previous studies, bonding at the metal-ceramic interfaces is accompanied by substantial charge transfer between metal and ceramic atoms [7],[21]. We calculated the Mulliken charges on all the atoms in the MTJ and plotted their distribution in the direction perpendicular to the interface in Fig. 4 for the O-terminated (a) and Al-terminated (b) MTJs. Usually, the oxide side acquires electrons and metallic atoms become positively charged. This is obviously the case for the O-terminated interface, where the oxygen O{1} layer tries to restore its favorable valence state by attracting electrons from the cobalt side. The four atoms of the Co{3} layer transfer +0.15 electrons per atom to the O{1} layer, where each of the three O atoms carries -0.86 charge. There is also an additional transfer of electrons from the Al{1} layer where each of the two Al atoms donates extra 0.2 electrons per atom to the oxygens in the O{1} layer in addition to the usual charge transfer to oxygens in the bulk alumina.

Fig.4. Layer-resolved charge distribution (average charge per atom) across the O-terminated and Al-terminated Co/Al$_2$O$_3$/Co MTJs. The interface boundary is marked by dotted vertical line.

The picture of the charge distribution across the Al-terminated interface (see Fig. 4b) is different from that in the O-terminated interface. Like in the bulk alumina, the interfacial Al{1} layer has an appreciable positive charge +2.42 (+1.21 per atom) due to sizeable charge transfer to the adjacent O{1} layer. This positive charge is screened very quickly within the Co layer as a result of the metallic character of interaction between the Co{3} and Al{1} layers. This screening is reminiscent of the Friedel oscillations since we also observe the charge alternation from plus to

minus and the interfacial Co{3} layer acquires a considerable negative charge of about -0.2 per atom. The transfer of electrons to the Co{3} from the Al{1} layer has further consequences in terms of interfacial magnetism and interfacial energetics. As a result of the charge transfer to the Co{3} layer we observe the reduction of the average magnetic moment within the Co{3} layer down to approximately 1.15 μ_B per atom. As can be seen from panel (e) of Fig. 2, the Fermi level lies above the majority d bands and the reduction in the magnetic moment is mainly due to the minority d band filling (compare with the bulk DOS shown in panel (f)).

The reduction of the surface magnetism results in lowering the interfacial work of separation which is defined as $W_{sep} = (E_{\text{Co}} + E_{\text{Al}_2\text{O}_3} - E_{int})/2A$. Here E_{int} is the total energy of the supercell containing the MTJ, E_{Co} and $E_{\text{Al}_2\text{O}_3}$ are the energies of the same supercell containing a single slab of pure Co and Al_2O_3, A is the area of the interface [21]. We found that within the spin-polarized total energy framework the work of separation for the O-terminated interface is equal to 6.35 J/m^2 and for the Al-terminated interface is equal to 3.64 J/m^2. In order to reveal the influence of magnetism on interfacial energetics, we have performed spin-restricted calculations for both terminations. It turned out that in the case of the O-terminated interface the difference between spin-polarized and spin-unpolarized values for the work of separation is less than 0.1 J/m^2. This result is not unexpected: the O-terminated MTJ and the single slab of pure Co have similar magnetic moments, therfore, the magnetic contributions to the total energy are subtracted in the work of separation since the alumina part of interface is nonmagnetic. However, in the case of the Al-terminated interface the quenching of the surface magnetism due to the charge screening effects costs $+0.7$ eV per interface and reduces the work of separation by 0.5 J/m^2 as compared to the spin-restricted value.

Spin-dependent tunnelling

Although we have not evaluated yet the conductance of the Co/Al$_2$O$_3$/Co junction, some conclusions about the mechanism of spin-dependent tunnelling can be made based on the LDOS considerations. The quantity which is relevant to the tunnelling is the LDOS at the Fermi energy across the insulating barrier. This quantity characterizes the decay of the evanescent metal-induced electronic states within the band gap of alumina and could, therefore, be used for elucidating the factors responsible for the spin polarization of the tunnelling current. We have performed an additional electronic structure calculation in which the thickness of the α-alumina insulating barrier in the O-terminated Co/Al$_2$O$_3$ structure was increased by 12 extra monolayers of alumina (i.e by the size of the conventional unit cell of bulk alumina).

Fig. 5a illustrates the behaviour of the LDOS at the Fermi energy for the majority and minority spin electrons as a function of the distance from the interface Co layer. Evidently, the LDOS decreases exponentially with the distance. Although the minority DOS is larger at distances near the interface, it decays more rapidly as compared to the majority LDOS. Eventually the majority LDOS starts to dominate over the minority LDOS resulting in the positive SP. This can be seen from Fig. 5b, which shows the SP of the DOS at the Fermi level as a function of the distance from the interface Co layer. The SP is defined by $(D_\uparrow - D_\downarrow)/(D_\uparrow + D_\downarrow)$, where $D_\uparrow$ and $D_\downarrow$ are the LDOS for the majority and minority spins respectively. It is clear from Fig. 5b,

the layer-averaged SP increases gradually without showing a tendency for saturation.

Fig. 5. The local density of states at the Fermi energy for the majority- (circles) and minority-
(squares) spin electrons (a) and the spin polarization of the DOS (b) as a function of the distance
from the interface Co layer.

In order to obtain quantitative information about the behaviour of the LDOS within the barrier,
we fitted the two curves presented in Fig. 5a by the exponential function $A \exp(-2\kappa z)$, where
A is the constant, z is the distance from the interface, and κ is the decay constant. We found
that $\kappa_\uparrow = 0.48$ Å^{-1} and $\kappa_\downarrow = 0.54$ Å^{-1} for the majority and minority spins respectively. This
corresponds to the decay lengths $l_\uparrow = 1.04$ Å and $l_\downarrow = 0.93$ Å. The decay constants determine the
height of the effective potential barrier $U = \hbar^2 \kappa^2 / (2m^\star)$. Assuming that the effective electron
mass $m^\star$ is equal to the free-electron electron mass, we obtain $U_\uparrow = 0.88$ eV and $U_\downarrow = 1.11$ eV.
It is not surprising that these values of the barrier height are lower than the values of $2 \div 2.5$ eV
extracted from experimental data (see, e.g. [2]), because LDA underestimates the band gap in
insulators.

Since $U_\uparrow < U_\downarrow$ the tunnelling current should become 100% positive spin-polarized in the limit
of large insulator thickness. This reflects the fact that the d-states of cobalt decay faster in the
insulator barrier that the s-p states. Such a behaviour was predicted by theory for epitaxially-
grown iron/semiconductor tunnel junctions [22]. In our case this conclusion might be precocious
since the analysis is based on the LDOS at the Fermi energy. It is well-known that electronic
states which correspond to different transverse momenta decay in the barrier with different
decay lengths. In the case of alumina which has a minimum direct band gap at the Γ-point, the

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electronic states with zero transverse momentum have the lowest effective barrier height and consequently the longest decay length. In addition to this, as was shown in Ref. [22], the bands which are characterized by different symmetry, i.e. associated with different angular character within the barrier, can have unequal decay lengths. We conclude, therefore, that in order to fully understand the factors controlling the SP, further calculations are necessary, which include the explicit evaluation of the conductance and its analysis in terms of contributions from the states with different transverse momenta and orbital characters.

Acknowledgments

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