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Oxygen-induced positive spin polarization from Fe into the vacuum barrier

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Bonding at the ferromagnet–insulator interface is an important factor which influences spin polarization of the tunneling current in ferromagnetic tunnel junctions. In this article we investigate the spin-polarized electronic structure of the (001) surface of body-centered-cubic iron covered by an oxygen overlayer, as this could reflect the mechanism of bonding and spin polarization in iron/oxide tunnel junctions. The Fe/O atomic structure is optimized using the plane-wave code CASTEP within the spin-polarized generalized-gradient approximation. The electronic structure and local densities of states are calculated using the linear muffin-tin orbital method. The results show hybridization of the iron $3d$ orbitals with the oxygen $2p$ orbitals, the strong exchange splitting of the former resulting in exchange-split bonding and antibonding oxygen states. These antibonding states are partially occupied for the majority spins but are almost unoccupied for the minority spins, which leads to a positive spin polarization in the density of states of the oxygen atoms at the Fermi energy. This positive spin polarization propagates from oxygen into the vacuum barrier. This is opposite to what is observed for clean Fe films, where the surface Fe layer has a negative spin polarization at the Fermi energy and remains negative into the vacuum. We infer that this $p-d$ bonding mechanism might be responsible for the experimentally observed positive spin polarization of the tunneling current from ferromagnetic metals through alumina. © *2000 American Institute of Physics.* [S0021-8979(00)54808-7]

The magnitude of magnetoresistance in magnetic tunnel junctions is determined by the spin polarization (SP) of the tunneling current.[1] Although within a simple approximation this spin polarization is determined solely by the density of electronic states at the Fermi energy in the ferromagnet,[2] more accurate considerations within a free electron model show that the potential barrier height can influence the magnitude and sign of the SP.[3] The SP can also be effected by the actual profile of the potential barrier[4] and the degree of disorder within the insulator.[5,6] The multiband description of the electronic transport problem demonstrates that the SP of the tunneling current depends strongly on the mechanism of bonding at the interface between the ferromagnetic metal and the insulator layer[7] and is characterized by the different decay lengths of evanescent Bloch waves in the barrier.[8] Studies of realistic band structures of Co/Al_2O_3[9] and Co/HfO_2[10] interfaces show that the SP of the density of states (DOS) at the Fermi level within the barrier changes sign compared to the SP in the bulk ferromagnet.

All these theoretical investigations demonstrate that the SP of the conductance in tunnel junctions is not an intrinsic property of the ferromagnet alone but depends on the electronic properties of the insulator and the ferromagnet–insulator interface. This fact was confirmed in recent experiments,[11] which found negative values of the SP of the tunneling current from Co across a $SrTiO_3$ barrier at low applied voltage. This is opposite to what is known for alumina spacers, where all ferromagnetic $3d$ metals display positive SP in tunneling measurements.[1] Experiments have also found both positive and negative SP depending on applied voltage.[12]

A full quantitative description of spin-dependent tunneling is a very complicated problem, since it should take into account the realistic atomic and electronic structure of the tunnel junction. Some insights on the mechanisms, which are responsible for the formation of SP, can, however, be obtained by considering the electronic structure of ferromagnet/vacuum interfaces. As was shown in Ref. 13, the electronic density of states within the vacuum barrier has negative SP for Fe, Co, and Ni, which reflects the negative SP of the DOS at the surface of these ferromagnets. In this article we investigate the influence of an oxygen overlayer on the (001) surface of body-centered-cubic (bcc) Fe on the SP of the DOS within the vacuum using first-principle calculations. We show that the presence of oxygen inverts the SP compared to that of the clean Fe surface. This supports the idea that the SP is very sensitive to the electronic structure of the ferromagnet/barrier interface.[7,9,10]

In order to simulate the Fe/O (001) surface we adopted a slab geometry consisting of 7 monolayers (ML) of the bcc-iron substrate film with the oxygen atoms placed in the fourfold hollow sites on both sides of the substrate. Structural optimization was performed using the pseudopotential plane-wave code CASTEP,[14] based on spin-polarized density functional theory within the generalized gradient approximation. Self-consistent calculations were performed using Vanderbilt ultrasoft pseudopotentials[15] with the nonlinear core corrections and a plane-wave energy cutoff of 300 eV. An equilibrium lattice parameter of 2.868 Å was predicted for bulk bcc Fe, which lies within 0.3% of the experimental value of 2.878 Å. A supercell geometry with periodic boundary conditions was applied in the calculations, using a (1×1) surface unit cell and a vacuum layer of 10 Å in the [001] direction. Relaxations were performed for the O atoms and the

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two surface layers of Fe, the three middle layers of Fe being fixed at their bulk positions. The Monkhorst–Pack k-point sampling scheme was used with a $7\times7\times1$ grid, which gives 10 k points in the irreducible Brillouin zone. The main result of the structural optimization is a very small equilibrium distance between the O layer and the surface Fe layer. This confirms the general observation of strong bonding between oxygen adsorbate atoms and the iron substrate.[16–19] We also find that the distance between the first and second Fe layers increases compared to the bulk value, which reflects the weakening of the bonding between the Fe atoms lying in the first and second layers. The detailed results of the structural optimization will be published elsewhere.

Using this relaxed atomic structure, the local DOS of the Fe/O (001) system was obtained by means of the spin-polarized scalar-relativistic linear muffin-tin orbital (LMTO) method[20] within the atomic sphere approximation (ASA) and von Barth–Hedin's exchange and correlation functional.[21] In these self-consistent calculations the substrate Fe film was extended to 13 ML by introducing additional 6 ML of Fe in the middle of the slab with the bulk interplanar spacing. In order to cover the vacuum space between the slabs, empty spheres were introduced. Their positions were chosen to belong to the symmetry group of the Fe/O (001) slab. The self-consistent calculations were performed by taking into account the muffin-tin orbitals of the s, p, and d angular momenta and using a grid of 56 k points in the irreducible Brillouin zone.

The resulting local densities of states are shown in Fig. 1 and are in good agreement with those of Ref. 17. The DOS of the inner Fe layer is similar to the bulk DOS of Fe, the magnetic moment being 2.23 μ_B. The DOS of the surface Fe layer is, however, very different from the bulk, which is the result of the reduced symmetry of the surface Fe layer and the covalent bonding between this Fe layer and oxygen. The bonding with oxygen does not quench the surface magnetism of the substrate, the magnetic moment of the surface, and subsurface Fe layers being 2.8 and 2.6 μ_B, respectively. This is reflected in the strong exchange splitting of the d band of the surface Fe layers. The surface Fe layer displays a pronounced peak in the DOS for the minority spin electrons at the Fermi energy E_F, which makes the SP of the DOS at E_F to be negative. This is similar to what has been found for the clean (001) surface of bcc Fe.[17]

The DOS of the oxygen layer has pronounced features in a 4-eV-wide distribution centered about 6.5 eV below the Fermi energy. These features are associated with the formation of the bonding states due to the covalent bonding between the $2p$ orbitals of oxygen and the $3d$ orbitals of Fe.[17,18] The bonding states display a splitting of about 0.6 eV, which is less than the exchange splitting of the d bands of the surface Fe layer, being about 2.6 eV. This is a consequence of the fact that the Fe d bands lie at higher energies and the splitting of the bonding states occurs via a second-order perturbation contribution. 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 3 eV above the Fermi energy. The exchange splitting of the d bands of Fe and the bonding between the d orbitals of Fe and

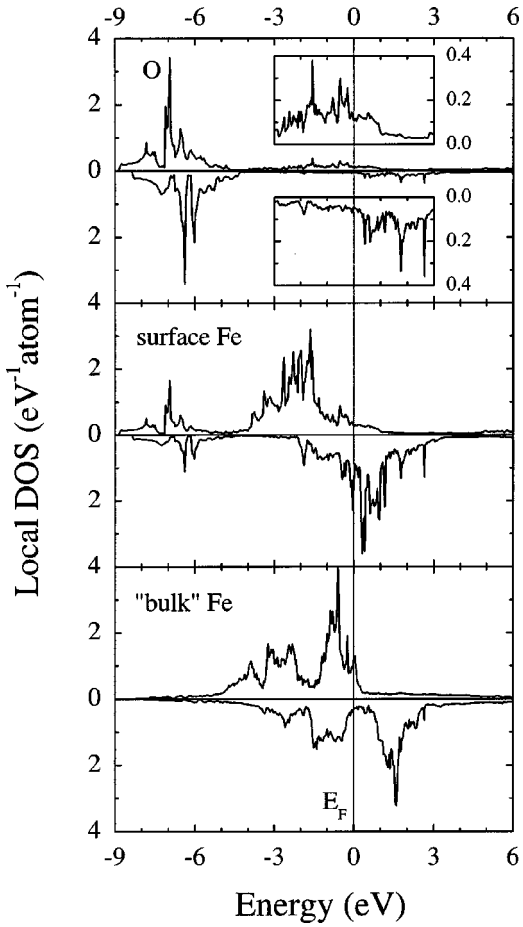

FIG. 1. Local densities of states of the Fe/O (001) slab as a function of electron energy. The Fermi level is denoted by the vertical line.

the p orbitals of oxygen induces a splitting of these antibonding states. Contrary to the bonding states, this splitting is large, mirroring the exchange splitting of the surface Fe d states. The antibonding states are partially occupied for the majority spins and are almost unoccupied for the minority spins. This leads to a positive spin polarization in the density of states at the Fermi energy and results in an induced magnetic moment of 0.2 μ_B on the oxygen sites.

The nature of the electronic states at the Fermi level is clear from Fig. 2, which shows charge- and spin-density contours of the states lying in the energy window from E_F-0.2 eV to E_F. As is seen from Fig. 2(a), there is not much charge density propagating from the O atom to the nearest Fe atoms, which reflects the antibonding character of the corresponding electronic states. As can be seen from Fig. 2(b), the spin density at the surface is dominated by the positive cloud extending outwards into the vacuum from the oxygen sites. This is opposite to the clean Fe surface, where the surface Fe layer has a negative spin polarization at the Fermi energy, which remains negative in the vacuum.[13]

The inversion of the SP due to the $p-d$ bonding between a $3d$ ferromagnetic metal and oxygen might be a general feature of the tunnel junctions based on alumina. According to experiments[22] the value of magnetoresistance has a threshold behavior as a function of the oxidation time, indicating the importance of O on the ferromagnet/insulator interface.

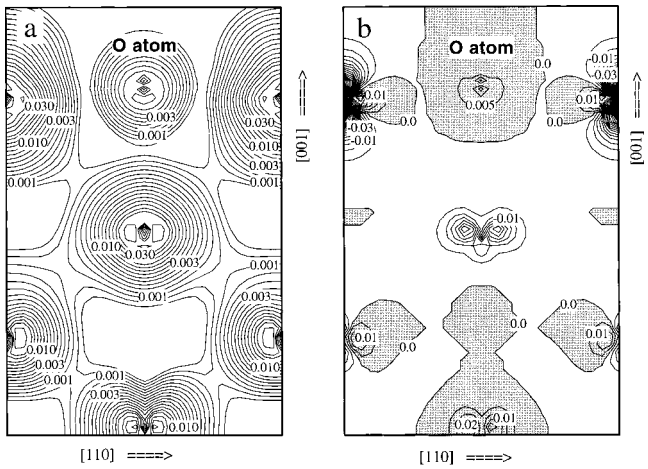

FIG. 2. Charge- (a) and spin-density (b) contours of the electronic states in the energy window from $E_F - 0.2$ eV to E_F in the (110) plane of the O/Fe (001) slab. Positive spin polarization in the spin density is indicated by shading.

Although the presence of Al in real Fe/Al_2O_3 tunnel junctions will modify the electronic properties of the ideal Fe/O interface considered in this article, we believe that the *sp* character of Als valence electrons will not influence dramatically the bonding between Fe and O and consequently the proposed mechanism of the inversion of SP. On the other hand, the low band gap and the strong contribution of the *d* character in $SrTiO_3$ insulator used in Ref. 11 may result in a significant change in the electronic properties at the ferromagnet/insulator interface due to the $p-d$ bonding between oxygen and Ti.

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