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Reversed spin polarization at the Co(001)-HfO₂(001) interface

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Ab initio electronic-structure calculations on the Co(001)-HfO₂(001) interface are reported. The spin polarization of conduction electrons is positive at the interface, i.e., it is reversed with respect to the spin polarization in bulk Co. The electronic structure is very sensitive to the interface structure; without atomic relaxations the reversed spin polarization is not found. The possible relation with spin-polarized tunneling and magnetoresistance is discussed. [S0163-1829(98)08448-3]

Recently magnetoresistive properties of junctions of ferromagnetic metals separated by an insulating barrier have attracted considerable attention.¹⁻⁴ The tunneling magnetoresistance of these materials is promising for applications like magnetic sensors and random-access memory elements.

The magnetoresistance is closely related to the spin polarization of the tunneling current through the insulating barrier. Tunneling experiments in the early seventies showed that the spin polarization was always positive for the 3*d* elements Fe, Co, and Ni,⁵ where positive means that there are more electrons of the majority spin direction at the Fermi energy than of the minority spin direction. This was surprising since electronic structure calculations showed a high density of states (DOS) of the minority *d* electrons at the Fermi energy, especially in Co and Ni.

Several semiquantitative explanations were given for the positive sign of the spin-polarization. One of the arguments was that primarily *s* electrons contribute to the conduction and that the *s* electrons have a positive spin polarization due to *s-d* hybridization.⁶ An exhaustive review on spin-polarized tunneling is given in Ref. 7.

In the past decade quantitative models on spin-polarized tunneling were developed. An example is the two-band model of Slonczewsky, which assumes spin-split free-electron bands in the magnetic metal.^{8,9} Very recently a more sophisticated treatment was used to calculate the DOS and the tunneling current of junctions of a ferromagnet, an insulator and a normal metal.¹⁰ The ferromagnet was modeled by a *spd* tight-binding fit to an accurate band structure of the bulk ferromagnet. The insulator was represented by two *s*-type tight-binding bands separated by a gap, while the non-magnetic metal was represented by a *s* band. It was shown that also the *d* electrons take part in the tunneling process and that this resulted in a negative spin polarization in the case of Co.

These models, though accounting for the basic elements in spin-polarized tunneling, i.e., a spin-split electronic structure of the ferromagnetic metal and a gap in the electronic structure of the insulating barrier, still suffer from a lack of an accurate description of the true crystal structure of the interface and its influence on the electronic properties.

We report *ab initio* calculations of structural and electronic properties of a Co-HfO₂ interface. We find that the spin polarization of conduction electrons at the interface is

positive. The crystal structure has an important influence on the electronic structure, i.e., without atomic relaxations the reversed spin-polarization is not found.

A Car-Parrinello related technique¹¹ was used to carry out atomic relaxations of the Co-HfO₂ interface. We have performed the structural optimizations using the *ab initio* total-energy and molecular-dynamics program VASP (Vienna *Ab initio* Simulation Program) developed at the Institut für Theoretische Physik of the Technische Universität Wien.¹² Electron-ion interactions were described using ultrasoft pseudopotentials as supplied by the Institut für Theoretische Physik.¹³ A plane-wave kinetic energy cutoff of 30 Ry was employed. Exchange and correlation were treated in the generalized gradient approximation (GGA) according to Ref. 14. The Brillouin zone integration was performed using a special mesh of 2 *k* points in the irreducible part, which was sufficient to calculate the atomic positions accurately.

In order to calculate details of the DOS many more *k* points should be used. Therefore the electronic structure was calculated with the far more efficient localized spherical wave (LSW) method,¹⁵ using approximately 200 *k* points. The LSW method makes use of the local density approximation (LDA). While GGA is more reliable in calculating equilibrium crystal structures, differences between LDA and GGA are relatively unimportant for the electronic structure.

Considering the interface between two materials from a calculational point of view, the first question is how well the lattice parameters match. In the case of Co and HfO₂ this is excellent for the fcc phases of both materials,¹⁶ the mismatch being less than 2%. The ground-state bulk crystal structure of Co is hexagonal close packed, but fcc Co exists as well, especially in thin films.¹⁷ The low temperature phase of bulk HfO₂ has a monoclinic crystal structure,¹⁸ the fcc structure being a high-temperature phase. However, the monoclinic structure is just a small distortion of the cubic crystal structure, the volumes per formula unit of these two phases being almost the same. Further, in our study the HfO₂ layer is very thin and has probably a crystal structure that is different from the structure of bulk HfO₂. Therefore we started the relaxation with the cubic structure. The main property of the HfO₂ layer is its insulating character, which is not affected by the restrictions on the unit cell.

The most simple direction to match Co on HfO₂ is the (001) direction for both materials. Translational symmetry in

the directions parallel to the interface was maintained by setting the a axis and the b axis equal to 3.548 \AA , the lattice parameter of Co. Each monolayer of Co contained two Co atoms while each monolayer of HfO_2 contained either one Hf atom or two O atoms. At the interface an O monolayer was stuck onto the top Co layer. The numbers of Co and HfO_2 monolayers were fixed at 5 and 7, respectively. These were repeated in the c direction to keep translational symmetry in all directions, resulting in a multilayered structure. This way the unit cell contained two Co- HfO_2 interfaces, which were kept equivalent by imposing mirror plane symmetry in both the central Co and HfO_2 monolayers. The volume of the unit cell was set to keep the sum of the subvolumes of the Co layer and the HfO_2 layer equal to the sum of their bulk volumes, resulting in a c axis of 18.17 \AA .

The crystal structure of the relaxed interface can be summarized as follows. The distortion from the bulk structure of fcc Co in the central Co monolayer is very small and also the central HfO_2 monolayer is very similar to the bulk structure. The monolayers at the interface are, however, strongly distorted. An important characteristic of the relaxed interface is the close approach of the Co and O atoms, leading to distances similar to those in the ionic materials CoO and Co_3O_4 . An extensive discussion on the crystal structure of the interface will be published elsewhere.¹⁹

Before discussing the electronic properties of the interface we briefly discuss the electronic structure of the separate constituents Co and HfO_2 . The calculated electronic structure of fcc Co is reported in Ref. 20. The main feature is the fully occupied majority d band, while the Fermi energy lies in the minority d band. Therefore the DOS at the Fermi energy is much lower for majority electrons than for minority electrons. The DOS of fcc HfO_2 is reported in Ref. 21. The valence bands are primarily formed by hybridized O $2p$ wave functions, while the conduction bands are primarily derived from Hf $5d$ (e_g) states. In our calculations the band gap is 5.5 eV .

To check the assumption that 5 ML of Co were enough for calculating interface properties without worrying about interference effects between the interfaces, the multilayer was extended with 2 ML of Co. Since the bulk crystal structure already was almost reached, the two monolayers were simply added at the center of the Co layer. From now on we will focus on the electronic structure of the system with 7 Co ML. The results showed that, although the central Co monolayer in the 5-Co-ML system did not show electronic properties completely identical to bulk Co, interface properties were already well converged with respect to the number of Co monolayers. This gives confidence that the atomic relaxation with 5 ML Co is a reliable model for calculating the interface structure.

In order to reveal the effects of the atomic relaxation on the electronic structure we first briefly discuss the electronic structure of the unrelaxed interface. The DOS in the central Co and HfO_2 monolayers is almost identical to the bulk materials. The electronic structure at the interface is altered for both Co and HfO_2 but the differences from the central monolayers are relatively small. The Co atoms at the interface still have a completely occupied majority d band and the DOS at the Fermi energy is still large for the minority spin direction. The O monolayer at the interface shows a very small density

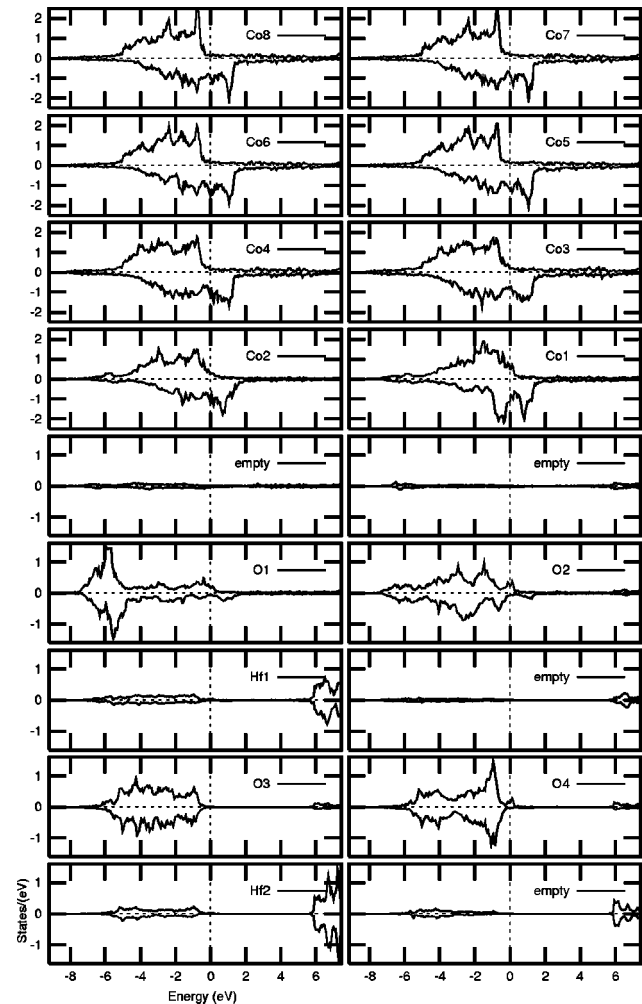


FIG. 1. Density of states per atom in the interface with 7 ML Co and 7 ML HfO_2 . The Fermi energy is at 0 eV . The DOS of the majority (minority) spin direction is shown at the positive (negative) axes. The plots with “empty” show the density of states in empty spheres, which were placed at large interstitial spaces.

of states in the gap region, due to Co wave functions extending into the insulating barrier. In the next monolayer of HfO_2 the DOS in the gap region is negligible, since the Co wave functions decay very fast. The spin polarization of electrons at the Fermi energy in the interface monolayers is negative, in agreement with the tight-binding calculations in Ref. 10.

The relaxed interface shows, however, very different electronic properties. See Fig. 1, which depicts the local DOS integrated over each atomic sphere. The central monolayer of Co is formed by the atoms labeled Co7 and Co8. This layer and also the next two monolayers (atoms Co3-Co6) show a bulklike DOS. The electronic structure of the Co atoms at the interface (atoms Co1 and Co2), however, is now essentially different from the bulk. The Fermi energy lies just below the top of the majority d band, i.e., at the interface the majority d band is not completely occupied anymore.

The two O atoms at the interface (O1 and O2) show densities of states very different from oxygen in bulk HfO_2 as well. Going deeper into the HfO_2 layer, the DOS becomes more like bulk HfO_2 and in the monolayer of Hf2 atoms the gap of approximately 5.5 eV is clearly visible. This shows

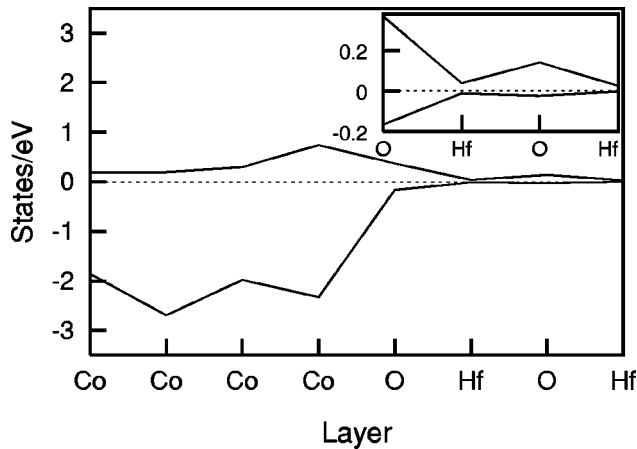


FIG. 2. Density of states per monolayer at the Fermi energy. The inset shows the density of states in the HfO_2 layers on a different scale.

that the seven monolayers of HfO_2 were sufficient to open a gap in the central monolayer, which again confirms the reliability of the calculation of interface properties. The appreciable DOS that persists in the gap region at the oxygen atoms near the interface, which is due to tails of the Co wave functions, is much larger than in the unrelaxed interface. Even in the next monolayers these tails are visible, as is most pronounced at the O4 atom. This feature is spin dependent because of the spin-dependent DOS of the Co atoms and because the decay of the Co wave functions into the barrier is spin dependent as well.

The spin dependence of the DOS near the Fermi energy has important consequences for the conduction electrons. Figure 2 shows the local DOS at the Fermi energy, integrated over each monolayer of atoms. Although the definition of a monolayer is somewhat loose, especially at the interface, it is clear that the spin polarization of conduction electrons in the HfO_2 monolayers near the interface is of opposite sign compared to the polarization in bulk Co. The tails of the Co d wave functions of the majority spin direction at the Fermi energy extend much farther into the HfO_2 layer than the minority spin direction.

The electronic bands in the c direction (perpendicular to the interface) show a much larger dispersion at the Fermi energy for the majority spin direction than for the minority spin direction (see Fig. 3). Therefore the interface does not merely show a much larger DOS at the Fermi energy for the majority spin direction, but the majority conduction electrons are also more mobile than the minority electrons. This will eventually result in a positive spin polarization of tunneling electrons.

An analysis of the wave functions shows the origin of the different dispersion of bands. The states of the majority spin direction near the Fermi energy are mainly formed by Co s, p, d_{z^2} states hybridized with O wave functions. The minority spin direction is dominated by Co-Co ($d_{x^2-y^2}$) interactions perpendicular to the stacking direction. Hence, in the region near the Fermi energy the majority spin direction predominantly contributes to the bonding between Co and O atoms. This is related to the strong magnetism of Co. At the interface the top of the d band has primarily d_{z^2} character,

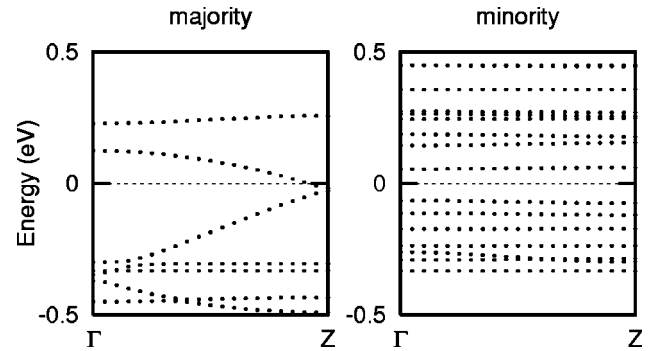


FIG. 3. Band structure of the interface with 7 ML Co and 7 ML HfO_2 near the Fermi energy in the c direction.

while at lower energies other d states dominate. Since the d_{z^2} states point in the direction of the stacking direction the majority spin direction is favored in the bonding between Co and O atoms near the Fermi energy.

To summarize, the interactions with O states near the Fermi energy of Co primarily take place via the majority spin direction. This leads to holes in the majority d band of the interface Co atoms and gives rise to a dispersion of bands near the Fermi energy, which is stronger for the majority spin direction. Due to the interactions the wave functions of the majority spin direction extend much farther into the insulating barrier than those of the minority spin direction. Therefore there are more majority electrons at the Fermi energy that are also more mobile in the direction perpendicular to the interface than the minority electrons. It could be possible that interfaces of strongly magnetic compounds and insulating oxides in general will show a positive spin polarization of conduction electrons. To validate this hypothesis *ab initio* calculations on interfaces between other ferromagnets, e.g., Ni, and other oxides, especially Al_2O_3 , are highly desirable.

The relaxed interface exhibits a region in the HfO_2 layer where the DOS at the Fermi energy is practically zero for the minority spin direction, while it is much larger for the majority electrons. This could be a key ingredient in magnetoresistive junctions of ferromagnetic metals and insulators. If successive ferromagnetic layers have parallel aligned magnetic moments the overlap between tails of wave functions in the barrier is larger than when they have antiparallel moments. Accordingly the resistivity of the antiparallel configuration is relatively high and could be switched to a lower resistivity by aligning the moments by an external magnetic field, resulting in negative magnetoresistance. This effect will be more pronounced the larger the spin polarization at the interface. Bulk materials with a truly 100% spin polarization at the Fermi energy are called half-metallic.²² It has been suggested that there is a relation between magnetoresistance and half-metallic properties in perovskite manganites^{23,24} and CrO_2 .²⁵ Spectroscopy and magnetoresistance experiments on junctions with very thin insulating barriers are therefore highly desirable as well.

In conclusion, we calculated the electronic structure of the $\text{Co}(001)\text{-HfO}_2(001)$ interface and found that the spin polarization of conduction electrons at the interface is opposite to that of bulk Co. This has consequences for the interpretation

of the spin polarized tunneling experiments performed in the early seventies, serves as a guide for present-day experimental physicists in the area of spin polarized transport, and shows the importance of atomic relaxations in calculations of the electronic structure of magnetic interfaces.

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