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Photoemission study of the Fe(001)/MgO interface for varying oxidation conditions of magnesium oxide

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The nature of interface bonding essentially determines the spin polarization of tunneling currents through ferromagnet/insulator interfaces. We focus on the influence of ultrathin *off*-stoichiometric MgO coverages on the spin-polarized electronic structure of the (001) surface of bcc-Fe. By applying a combination of low-energy spin-resolved and core-level photoelectron spectroscopy, we show that the MgO stoichiometry has a direct impact on the interfacial spin polarization. The results underline the importance of controlling the chemical composition and bonding at ferromagnet/oxide interfaces to further optimize spin-dependent tunneling devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2711418]

In recent years, spin-dependent tunneling in ferromagnet/insulator/ferromagnet structures has aroused enormous attention not only due to prospective large-scale applications in magnetic tunnel junctions (MTJs) but also for a renewed fundamental interest in understanding the complex physics of spin-dependent transport.[1] In general, spin-dependent tunneling is acknowledged to be an extremely interface-sensitive phenomenon. The ferromagnet-insulator (FM/I) boundary is thus a critical factor in determining and controlling the magnitude of the spin polarization P in MTJs. Depending on how the ferromagnet and insulator are forming bonds at the interface, the tunneling spin polarization is primarily determined by the electronic and atomic structure of the electrode/barrier interface.[2]

Within the picture of a model-quasiperfect MTJ system, such as Fe(001)/MgO/Fe and related multilayers, a negligible interaction between ferromagnet and insulator at the interface is predicted theoretically.[3] This fact has been confirmed by recent experiments, which found a conservation of the spin-split electronic structure of Fe covered by an ultrathin insulating MgO layer.[4,5]

Beyond the rather idealistic assumption of perfect ferromagnet/insulator interfaces, the consideration of realistic junctions leads to a situation with quickly increasing complexity. Several groups reported on the presence of an FeO layer, which is formed between the Fe and MgO layers.[6] The tunneling current, usually governed by majority electrons of Δ_1 symmetry, is thereby substantially reduced.[7] This effect is attributed to the bonding between Fe and O, which redistributes the majority Δ_1 density of states from the interface region to the in-plane Fe–O bonds.

Despite strong evidence for the key role played by the electronic properties at the FM/I interface, little is known about the influence of an *off*-stoichiometric MgO barrier. Depending on an excess or deficiency of oxygen atoms at the MgO interface, different bonding conditions will result in a modification of the spin-split ferromagnetic electronic structure, which in turn is supposed to determine noticeably the tunneling efficiency.

In view of this apparent interface sensitivity, our investigations focus on the electronic properties of Fe/MgO interfaces with varying oxidation conditions of MgO. The interface chemical environment was characterized by core-level photoelectron spectroscopy, whereas the electronic structure was explored on the basis of low-energy spin- and angle-resolved photoemission spectroscopy (PES). In this article, we show that the stoichiometry of the MgO barrier has a direct impact on the interfacial spin polarization. In case of oxygen-deficient Fe(001)/MgO systems, an enhancement of the positive spin polarization at the Fermi energy E_F is observed, whereas an oxygen-rich interface is characterized by a reduction of interfacial spin polarization.

Prior to the PES experiments, Fe(001)/MgO samples were prepared *in situ* by molecular beam epitaxy under ultrahigh vacuum conditions onto GaAs(100) substrates, which had been treated by two successive cycles of Ar^+ sputtering and annealing to 840 K. This procedure ensured a (4×6) reconstruction of the GaAs(100) surface, which was verified by low-energy electron diffraction (LEED). Subsequently, 27 monolayer (ML) thick Fe(001) films were deposited at 400 K with a growth rate of about 3 ML/min. The bcc structure of the Fe layers was confirmed by LEED. Each preparation step was followed by Auger electron spectroscopy (AES) and no traces of oxygen or carbon were found within the detection limit before and after Fe deposition. Finally, ultrathin MgO layers 1 (ML) were deposited by evaporating Mg from grain material in a variable oxygen backpressure.

Information on the interface chemistry was obtained from monitoring the chemical shifts of the Fe 3p and Mg 2p core levels at a photon energy of $h\nu$=88.3 eV, thereby ensuring a very high surface sensitivity. For the first set of samples, labeled (S1), Mg was deposited with minimal additional oxygen supply ($p_{O_2} < 2\times 10^{-9}$ mbar), resulting in an oxygen-deficient MgO composition. The corresponding

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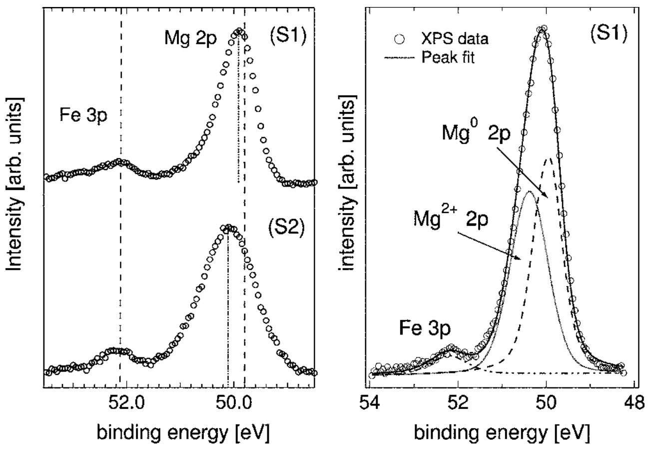

FIG. 1. Left: Core-level photoemission spectra of the Mg 2*p* and Fe 3*p* levels recorded at a photon energy of $h\nu=88.3$ eV for oxygen-deficient MgO layers (S1) and subsequently oxidized MgO (S2). Right: The oxygen-deficient Mg 2*p* peak was fitted by two Lorentz-Gaussian sum curves for the Mg^{2+} and Mg^0 levels.

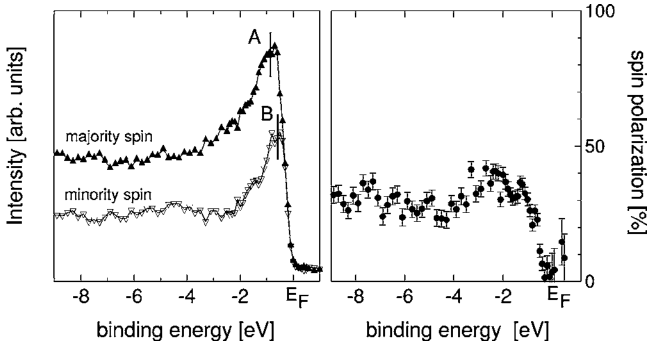

FIG. 2. Spin-resolved photoemission spectrum of the 3*d* valence states of an uncovered Fe film recorded at a photon energy of $h\nu=39.2$ eV [▲ denotes majority electrons (↑), ▽ denotes minority electrons (↓)].

background-corrected photoemission spectrum, displayed in Fig. 1, verifies the partial oxidation of the Mg layer due to the leftward shift of the Mg 2*p* peak center to a higher binding energy E_B relative to the Mg^0 2*p* level at E_B (Mg^0) $=49.8$ eV. The oxidation ratio of Mg^{2+}/Mg^0$\approx 0.5/0.5$ was quantified by applying a standard least-squares fit procedure of symmetric Gaussian/Lorentzian line shape (Fig. 1). The Mg^0 peak position thereby was fixed to $E_B=49.8$ eV, whereas the remaining parameters, Mg^{2+} position, relative intensity, and full width at half maximum (FWHM), were allowed to vary within reference-based intervals.[8] Furthermore, the unshifted position of the Fe^0 3*p* level indicates that no oxidation of the Fe interface layer has taken place.

An oxygen excess at the Fe/MgO interface was generated when the deposition of Mg was followed by a subsequent oxygen exposure of 1.2 L ($1\ \mathrm{L}=10^{-6}$ Torr s) [sample type (S2)]. A complete oxidation of Mg atoms is achieved, as visualized by the chemical shift of the Mg peak maximum towards the Mg^{2+} 2*p* level and the broadening of linewidth (Fig. 1). Moreover, a leftward shift of the Fe 3*p* peak indicates the presence of partially oxidized Fe 3*d* levels within the Fe surface layer. This finding stands in agreement with theoretical and experimental studies which found that during adsorption of low oxygen coverages, O_2 molecules spontaneously dissociate on the sample surface and partially incorporate below the Mg top layer.[9]

Our aim is to relate the chemical environment at the Fe(001)/MgO interface to potential modifications of the Fe 3*d* electronic structure. Thus, spin- and angle-resolved photoemission experiments were performed at a low photon energy ($h\nu=39.2$ eV) at the beamline U250-PGM of the storage ring DELTA (Germany). The kinetic energy of the photoemitted electrons together with their spin polarization was directly measured in an electron spectrometer with integrated low-energy electron diffraction spin-polarization detector (SPLEED). By exciting the Fe electronic states in Γ-Δ-H direction with linear *p*-polarized light and collecting the photoelectrons in normal emission, the allowed interband transitions are restricted by symmetry considerations to Δ_1 and Δ_5 initial states, with the photoelectrons being excited into Δ_1 final states.[10] The spin polarization component *P* was measured along the magnetization direction.

The basic concept of a spin-polarized PES experiment with ultraviolet light permits one to resolve changes of the interfacial Fe 3*d* electronic states even through a MgO overlayer, since valence band spectral contributions from MgO appear below its band gap.[11,12] It is worthwhile to point out that due to a small mean free path of the collected photoelectrons, the PES experiment is most sensitive to the Fe 3*d* electronic states in contact with MgO, which play the important role in the tunneling efficiency.

To compare the spin-resolved electronic structure of an uncovered Fe(001) film to that of an Fe(001)/MgO interface, the photoemission spectra of a 10 ML thick Fe(001) film as well as the corresponding spin asymmetry are shown in Fig. 2. The electronic structure near the Fermi level is entirely dominated by the Fe 3*d* bands, which are characterized by two neighboring features: The first peak located just below the Fermi level at −0.4 eV (labeled B) and a second structure at −0.9 eV (labeled A). We assign these contributions to minority (↓) and majority (↑) spin bands of $\Delta_5^{\downarrow}$ and $\Delta_1^{\uparrow}$ symmetries, respectively. The typical spin asymmetry was found to be positive with a magnitude of the order of $P\sim 30\%-40\%$ after correction of the secondary-electron background.

In the following, we will focus on the modifications of the Fe 3*d* valence bands in contact with MgO. We investigated the spin polarization of Fe layers covered by oxygen-deficient MgO layers as well as Fe/MgO interfaces with a surplus of oxygen atoms. In Figs. 3(a) and 3(b), the spin-resolved PES spectra of samples corresponding to these two scenarios are displayed. At first sight, the comparison with an uncovered Fe layer indicates additional spectral features of the O 2*p* levels (labeled C) below 3.5 eV binding energy. Moreover, the Fe 3*d* states close to the Fermi level exhibit significant modifications compared to the uncovered Fe film.

In the case of the *oxygen-deficient* MgO overlayer (S1), a clearer separation of spectral weights of the $\Delta_5^{\downarrow}$ and $\Delta_1^{\uparrow}$ features is observable in Fig. 3(a), which leads to an enhanced spin polarization below the Fermi level E_F. This unexpected increase of *P*, exceeding values of 50%, can be qualitatively understood on the basis of the spatial orientation of electronic states at the oxygen-deficient interface.

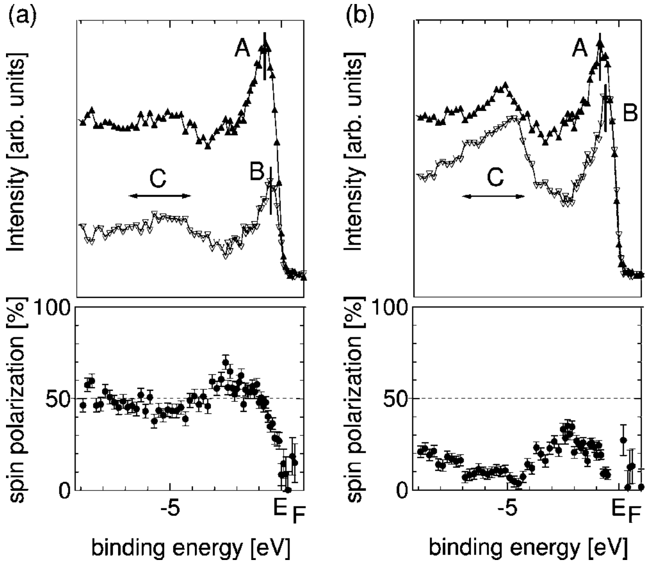

FIG. 3. Photoemission spectra for the Fe 3d states at the FM/I interface in contact with (a) an oxygen-deficient MgO interface layer (S1) and (b) subsequently oxidized MgO (S2), recorded at a photon energy of $h\nu$=39.2 eV [▲ denotes majority (↑) electrons, ▽ minority (↓) electrons].

Since the Fe 3d $\Delta_1^{\uparrow}$ state is characterized by s, p_z, and d_z^2 wave function symmetries, whose orbitals point toward the insulator, a large electronic interaction with MgO becomes possible. On the opposite side of the interface, the MgO surface is partially carrying oxygen vacancies of Δ_1 character, which—like occupied oxygen positions—are located on top of the Fe atoms. Recent scanning tunneling microscopy and spectroscopy experiments on ultrathin MgO(001) layers deposited on Ag(001) located an oxygen vacancy ground state just −1 eV below the Fermi level.[13,14] As a consequence, interface hybridization of the $\Delta_1^{\uparrow}$ oxygen defect bound state with the Fe 3d $\Delta_1^{\uparrow}$ level seems reasonable and may result in an increased spin polarization below the Fermi level.

In the case of an oxygen *excess* at the Fe/MgO interface (S2), the electronic structure near the Fermi level undergoes a converse modification. As displayed in Fig. 3(b), we observe a convergence of photoemission contributions of the Fe 3d $\Delta_5^{\downarrow}$ and $\Delta_1^{\uparrow}$ bands, leading to a noticeable reduction of the spin polarization to a value $P < 30\%$. The partial oxidation of the Fe surface layer might therefore be accompanied by a decrease of the interfacial polarization. This result is in qualitative agreement with theoretical calculations,[7] which predict a decrease of the Δ_1 majority density of states at the Fe/FeO/MgO interface due to an in-plane bonding between the surface Fe and oxygen atoms positioned in the bcc hollowsites.

In summary, we presented a combined study of core-level and spin-resolved valence band photoemission spectroscopies, which relate the chemical environment of the Fe/MgO interface to bonding-induced modifications of the interfacial Fe 3d electronic structure. By capping the Fe(001) surface with oxygen-deficient MgO layers, an enhancement of P close to E_F is observed, whereas a surplus of oxygen atoms at the interface leads to a partial oxidation of the Fe layer followed by a reduced value of P. The results clearly emphasize the critical role of interface bonding and suggest that the spin polarization of tunneling devices may be made tunable by chemical engineering of the FM/I interface.

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