The Fe/MgO Interface: The Important Role of Oxygen

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IFF-9: Electronic Properties

Utilizing spin and angle-resolved valence band photoemission spectroscopy, we systematically studied the effect of an oxygen excess or deficiency on the electronic band structure at the interface of Fe/MgO(001). Our data revealed a multifaceted modification of the spin polarization at the Fermi level that we can ascribe to the different nature of the oxygen bonding. The most prominent observation, a strong enhancement of the spin polarization in the case of an oxygen depletion at the interface, may be exploited to further improve the functionality of single crystalline magnetic tunnelling junctions (MTJs).

Due to their manifold application potential, e.g. in magnetic data storage technology (read heads of hard discs, non-volatile magneto-resistive random access memory), the further development of MTJ's functionalities is in the focus of current spintronic research. Today, MTJs based on single crystalline Fe(100)/MgO or Co(100)/MgO systems provide the highest achievable tunnelling magneto-resistance (TMR) ratios. The progress compared to amorphous MTJs is related to an utilization of the MgO tunnelling barrier as a spin filter. This new functionality is associated with different conductivities of the electron wave functions in the gap of the tunnel barrier that depend on their spatial symmetry character. It is thus obvious that the interfacial band structures in MTJs will have a strong influence on their spin dependent transport properties. For the theoretical calculation of high TMR ratios in single crystalline Fe/MgO/Fe MTJs an atomically sharp and perfectly ordered interface is often assumed. In contrast, a realistic interface may suffer upon morphological and chemical deviations from ideality. One resulting consequence is an ongoing discussion about the formation of FeO and its influence upon the maximum obtainable TMR value. For an asymmetric system, Fe/FeO/MgO/Fe, the charge redistribution due to the iron oxide formation was predicted to drastically reduce the TMR ratio[1], while Tusche et al. [2] predicted high TMR values for a symmetric Fe/MgO/Fe MTJ with one monolayer of FeO at both interfaces. Our spin polarized photoemission study aims to clarify the influence of a chemical modified interface upon the electronic band structure and its consequences for the spin polarization at the Fe/MgO interface.

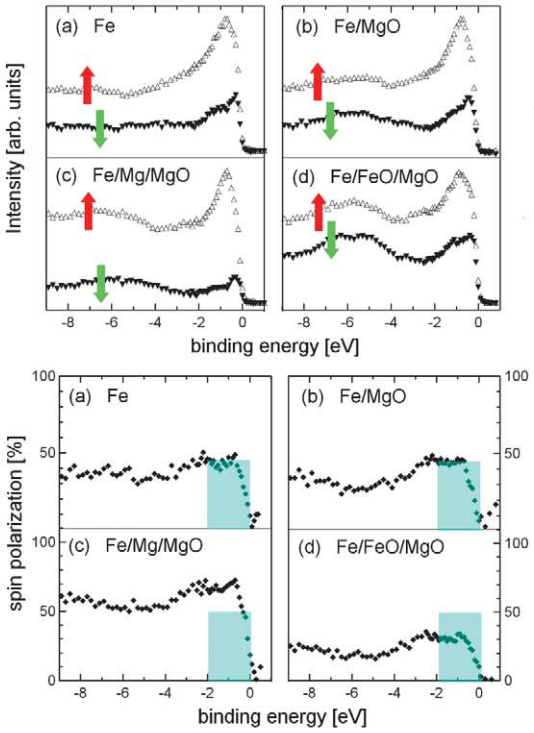

FIG. 1: Spin-resolved photoemission spectra(top) and spin polarization(bottom) for (a) pure Fe surface, (b) stoichiometric, (c) underoxidized and (d) overoxidized Fe/MgO(001) interface. The spectra were collected in normal emission. Non-relativistic dipole selection rules allow transitions from initial states with Δ_1 and Δ_5 spatial symmetry. Filled/open triangles display spin down/up photoelectrons. The underlying light blue rectangles represent the spin polarization of the pure Fe surface.

For this purpose, three different sample classes were prepared representing a stoichiometric (Fe/MgO), underoxidized (Fe/Mg/MgO) and overoxidized (Fe/FeO/MgO) MgO film at the interface. Special emphasis was laid on the chemical characterization of the MgO/Fe interface. Besides Auger electron spectroscopy, the degree of Mg and Fe oxidation was supervised by probing the chemically induced shifts of the Mg 2p and Fe 3p core levels, thereby using a photon energy of 88.3 eV to ensure high surface sensitivity. A more detailed description of the preparation procedure and experimental geometry is given in [3]. The spin and angle-resolved pho-

toemission spectra were recorded at the beamline U250-PGM operated by the research centre Jülich at the storage ring DELTA (Dortmund) using a cylindrical mirror-type analyzer with integrated spin polarized low-energy electron diffraction detector (SPLEED).

Fe-system: The photoemission spectra always reveal two peaks, one is located at (-0.4 ± 0.2)eV below the Fermi energy and the other at (-0.9 ± 0.2)eV binding energy. They originate from bulk Fe initial states with Δ_5 and Δ_1 spatial symmetry. For uncovered Fe films, a positive spin polarization of about 40% to 50% in an energy interval from -0.2 eV to E_F was obtained (Fig. 1a).

Fe/MgO system: Besides the peak formation in the range of -3.5 to -8.5 eV, originating from oxygen 2p levels, the spectra and the spin polarization (Fig.1b) do not display noteworthy differences when we study stoichiometric MgO films in contact to the Fe electrode. This observation reflects the strong ionicity of the MgO bonds which allows no reaction with the adjacent metal.

Fe/FeO/MgO system: The spectral intensities originating from the Fe Δ_5 and Δ_1 states approach each other, leading to a reduced spin polarization of about 30% (Fig.1d). Moreover, the spin resolved measurements displayed a spin-splitting in the oxygen-related features that we associate with FeO formation (Fig.2). We thus conclude that the partial oxidation of the Fe surface layer is accompanied by a reduction of the spin polarization at the interface. Our conclusion is consistent with theoretical calculations that predict a strong decrease of Δ_1 majority density of states at the interface. The reduction is caused by an increased in-plane bonding between the surface Fe and oxygen atoms positioned in the bcc hollow-sites.

Fe/Mg/MgO system: Our spectra display a gain in intensity for the direct transitions emerging from initial states with Δ_1 symmetry and spin up character when compared to those with Δ_5 symmetry and opposite spin. The resulting effect is a strong enhancement of the spin polarization close to the Fermi level, exceeding a value of 70% (Fig.1c). These systems possess an excess of metallic magnesium atom with two uncombined valence electrons.

For MgO, having only a low content of unbounded Mg atoms, it is known that strongly localized defect states will develop in the bandgap, so called oxygen vacancies or F-color centers. In our samples, the oxygen vacancy concentration is high: (Mg^{2+}/MgO $\sim$ 0.5). As a consequence, these oxygen vacancy states may interact with each, e.g. form defect bands. Furthermore, the symmetry of the localized defect states has been calculated to exhibit a Δ_1 spatial symmetry character [4]. Recent performed scanning tunneling spectroscopy and microscopy (STS/STM) experiments on ultrathin MgO(001) layers deposited on Ag(001) gave evidence for a ground-state of the oxygen point defects beeing located around -0.1 eV below the Fermi level [5]. Based on these findings we may consider, that an extended oxygen vacancy concentration may form an Δ_1-like electronic state with a band-like character in the energy region close to E_F. Using this assumption, the presence of extended oxygen vacancies at under-oxidized Fe/MgO interfaces may involve a hybridization between Δ_1-like oxygen defect states with the Fe 3d $\Delta_1^{\uparrow}$ valence bands. Our observed increased spin polarization close to E_F would then be consistent within this qualitative model.

Recent electronic transport calculations, performed by Velev et al. [6], predicted that oxygen point defects located in the middle of a thin MgO film will lead to a strong reduction of the TMR values, because they will establish a spin-independent conduction channel between the two electrodes. Expanding these findings, we conclude that not only the existence/density of uncombined Mg but also its position in the barrier will have a decisive influence upon the performance of MTJs. According to the model proposed above, we suppose that the enhancement in the functionality of MTJs should be most effective, if the oxygen vacancies are located only at the Fe/MgO interface.

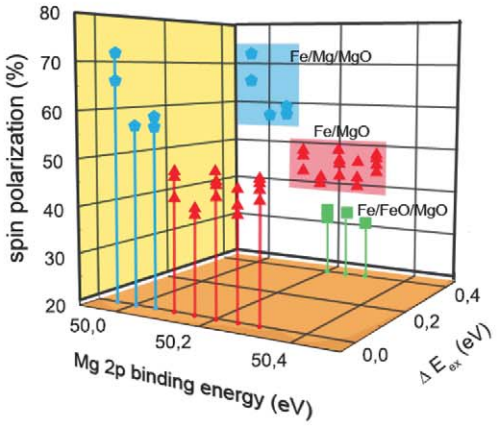

FIG. 2: Spin polarization (SP) at the Fermi level E_F for the systems Fe/Mg/MgO (blue pentagrams) and Fe/MgO (red triangles) as a function of the binding energy of the Mg **2p** peak maximum. The Fe/FeO/MgO samples (green rectangles) are characterized by an additional exchange splitting ΔE_{ex} in the O **2p** levels.

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