Interfacial Resonance State Probed by Spin-Polarized Tunneling in Epitaxial Fe/MgO/Fe Tunnel Junctions

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The direct impact of the electronic structure on spin-polarized transport has been experimentally proven in high-quality Fe/MgO/Fe epitaxial magnetic tunnel junctions, with an extremely flat bottom Fe/MgO interface. The voltage variation of the conductance points out the signature of an interfacial resonance state located in the minority band of Fe(001). When coupled to a metallic bulk state, this spin-polarized interfacial state enhances the band matching at the interface and therefore increases strongly the conductivity in the antiparallel magnetization configuration. Consequently, the tunnel magnetoresistance is found to be positive below 0.2 V and negative above. On the other hand, when the interfacial state is either destroyed by roughness-related disorder or not coupled to the bulk, the magnetoresistance is almost independent on the bias voltage.

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The tunnel magnetoresistance (TMR) effect is widely studied not only due to the large-scale applications of the magnetic tunnel junctions (MTJs) [1] but also for the understanding of the complex physics of spin dependent transport. By using epitaxial growth techniques, one can "engineer" model-quasiperfect MTJ systems, in which theory and experiment may confront each other. After a series of pioneering results on the tunnel transport in epitaxial systems [2], a couple of nontrivial physical effects, predicted by theoretical calculations, have experimentally emerged. One could cite the magnetic coupling mediated by tunneling of electrons [3] or, beyond the free electron framework, the influence of the realistic electronic structure of the electrodes on the tunnel transport [4,5]. Recently, *ab initio* calculations [6–8] performed on epitaxial MTJ systems have shown that the deviations of the wave function from a single plane-wave form and of the Fermi surface from a sphere, related to the anisotropy of the electronic properties in the reciprocal space, are crucial for the physics of tunneling. In particular, a totally counterintuitive result, directly driven by the influence of the interfacial resonant states on the tunneling, showed that electrons with nonzero quasimomentum parallel to the interface could have a larger probability to tunnel compared to those with zero parallel quasimomentum. Moreover, very large TMR ratios have been theoretically predicted in single crystalline MTJs, namely, Fe/MgO/Fe. They are determined by the different tunneling mechanisms and symmetry-related decay rates of the Bloch waves for the majority and the minority spin channels. Roughly, an emitter monocrystalline ferromagnetic (FM) electrode filters in terms of symmetry the electrons subsequently injected across the insulating (I) barrier. The tunnel transport probes: (i) the differences in spin injection (extraction) efficiency (directly related to the interfacial FM/I matching/coupling) and (ii) the differences in decay rates when tunneling across the barrier. Consequently [6,7], for large MgO thickness, in the asymptotic regime, the tunneling is found to be governed by a majority spd-like character state Δ_1. The conductance in the antiparallel (AP) configuration is very low (almost zero). The spin asymmetry is predicted to increase above 1000%. On contrary, when the thickness of the insulating layer decreases, the contribution of the double degenerate pd character state Δ_5 becomes significant, the conductance in the AP state increases, and therefore the TMR ratio decreases. Moreover, the tunnel transmission becomes strongly affected by resonant effects either at the interfaces [6–9] or in the barrier [10]. For the Fe(001)/MgO interface, a peak in the interfacial minority density of states (DOS) is found above the Fermi energy. It is related to an interfacial resonance (IR), arising from an effect of electronic confinement between the bulk and the barrier where the electronic wave is evanescent. The IR states from both sides of the barrier may couple to each other, leading to a resonant tunneling mechanism [8] which manifests itself as spikes in the conductance distribution in particular $k_{\parallel}$ points in the two-dimensional Brillouin zone. The width of these spikes is determined by the strength of the coupling in the barrier, which decreases exponentially with the barrier thickness. Consequently, the conductance from an IR state is particularly important for thin barriers. Alternatively, as shown in this Letter, the contribution to the tunneling of an interfacial state may be activated by biasing the junction at finite bias voltage.

In this Letter, we show that spin-polarized tunneling transport in high-quality MTJs can be used as a probe for the IR states in the Fe(001)/MgO system. Experimentally, the IRs are "controlled" via the topological quality of the Fe/MgO interface, perfectly monitored by the epitaxial growth of the layers. Atomically flat Fe/MgO interfaces provide IRs, located in the minority spin bands. When these resonances get "activated," the increase in the interfacial spin-polarized DOS compensates the spin filtering in the electrodes and reverses the

sign of the magnetoresistance. This explains the bias-voltage variation of the experimental TMR, observed to be positive below 0.2 V and negative above. However, in systems where the interfacial state is either not coupled to the bulk or destroyed by interfacial disorder, we observe that its contribution to the tunneling is annihilated. In this case, the magnetoresistance is observed to be always positive and almost independent of voltage, as expected for the symmetry of the electrons filtered by the Fe monocrystalline electrodes and by the MgO insulating barrier.

In order to support our experimental data, we calculated the electronic structure of the Fe/MgO/Fe stack with the Full Potential-Linear Augmented Plane-Wave WIEN2K code [11], using a supercell consisting of ten Fe layers, sandwiched in between six MgO layers. To describe a "realistic" Fe/MgO interface of an experimental junction, a complete monolayer of O has been alternatively considered at 0.4 Å above the interfacial Fe, in the surface Fe hollow site [12]. The calculation is performed within a full potential framework, without any empty sphere in the interstitial. We found a gap of about 6.8 eV for the outer MgO layer (fair description of bulk MgO E_g = 7.8 eV), whereas, in the middle of the slab, bulklike properties are found for the innermost Fe layer. In agreement with previous calculations [6,13,14], we find an IR state located in the minority d_{z^2} orbital, belonging to a Δ_1 symmetry (s, p_z, d_{z^2}) band of the interfacial Fe for both Fe(001)/MgO and Fe/Fe-O/MgO systems [Fig. 1(a)]. This IR gets slightly shifted upwards in energy, when the complete O monolayer is introduced between the Fe and MgO, in the surface Fe hollow site. However, the presence of the Fe-O layer does not alter the effect of the resonant state in the tunnel transport, because this state lies in the minority d_{z^2} vertical orbitals of the surface Fe and these electrons are not affected by the bonding between Fe and O. The O has only planar bonding via the in-plane s, p_x, p_y orbitals with the surface Fe atoms. Moreover, the vertical bonding of O with the subsurface Fe via O_{p_z}-$Fe_{d_{z^2}}$ orbitals does not affect the surface resonance. In order to uncouple the interfacial state from the bulk DOS of the bottom electrode, we have used a Pd/Fe/MgO/Fe/Co structure with a rather thin Fe bottom layer. The bulk electronic structure of Pd is illustrated in Fig. 1(b). One can observe that slightly above the Fermi energy the DOS vanish abruptly. Although the epitaxy conserves the Δ_1 symmetry from the bcc Fe in the fcc Pd, beyond 0.2 eV above the Fermi energy the only remaining band in Pd is a dispersive Δ_1 symmetry, one which shows mainly s and p character. Thus, one can immediately see that the d_{z^2} IR in Fe finds no similar orbital character in Pd. This leads to a "filtering effect," directly related to the orbital character "mismatch" of the electronic bands above E_F, between Fe and Pd, and affects drastically the propagation of the Bloch

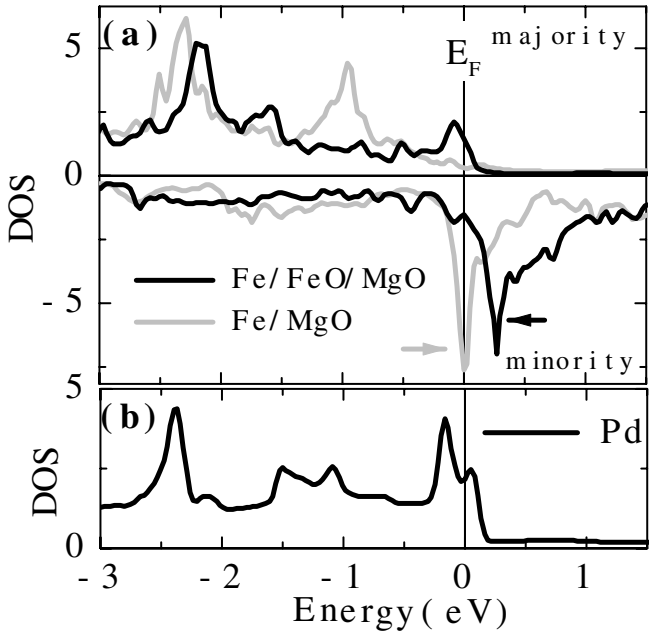

FIG. 1. (a) Calculated local spin-polarized DOS for the interfacial Fe in Fe/MgO/Fe and Fe/FeO/MgO/Fe stacks. The arrows indicate the IR in the minority DOS of Fe. (b) The total DOS of bulk Pd.

waves coming from the Fe side for electrons having a coherence/spin diffusion length larger than the thickness of the bottom Fe.

Our MTJ multilayer stacks are grown [15] by molecular beam epitaxy (MBE). Two distinct sets of samples have been elaborated, both on MgO substrates annealed at 500 °C for 20 min. For the first set, labeled (S1), a first 50 nm-thick Fe layer is deposited at room temperature (RT) using a Knudsen cell, then annealed at 450 °C for 15 min in order to smooth its surface and to induce a perfectly flat bottom Fe/MgO interface. For the second set of samples, labeled (S2), we introduce a 40 nm-thick Pd buffer, flattened by annealing at 400 °C, in between the substrate and a 2 nm-thick bottom Fe electrode. During the entire growth of this 2 nm Fe layer, a two-dimensional (2D) layer-by-layer growth is asserted by reflection high energy electron diffraction (RHEED) intensity and in-plane lattice parameter oscillations. The similitude of the bottom Fe electrode quality in both sets of samples is furthermore confirmed by RHEED (small scale) and *ex situ* atomic force microscopy analysis. Furthermore, on both set of samples, onto the bottom flat Fe electrode, a nominal 2.5 nm MgO insulating layer is subsequently deposited at room temperature using an electron gun. We observe again the 2D layer-by-layer growth of MgO up to 10 to 15 monolayers, asserted by the oscillations of RHEED intensity and in-plane lattice parameter. The continuity of the insulating MgO layer and its pseudomorphic epitaxial growth on Fe were checked down to 0.6 nm thickness, at different spatial

scales, as shown in our previous studies [3,15,16]. We point out that the pseudomorphic epitaxial growth of MgO on Fe is a key parameter for the conservation of symmetry from the Fe electrode through the MgO barrier (conservation of $k_{\parallel}$). This has a huge impact on the Bloch wave propagation in the stack. Finally, on the top of the MgO barrier, a second magnetic electrode is epitaxially grown. It consists on a bilayer composed of a 5 nm-thick Fe layer, magnetically hardened by 10 nm-thick Co layer. However, as confirmed by the RHEED analysis for both sets of samples, the growth of the top Fe electrode onto the MgO leads to a rough top MgO/Fe interface. This affects drastically the interfacial electronic structure of the top Fe, for which the IR is destroyed by the disorder. Lastly, the sample is capped with a 10 nm Au layer.

Magnetotransport properties of the MTJ have been measured at RT [17] in 20 μm micrometric-size junctions patterned by UV lithography and Ar ion etching [15]. In Fig. 2 we illustrate the tunnel magnetoresistance curves as a function of the bias voltage, measured for the two samples issued from set (S1) and set (S2). The amplitude of the TMR presented here is moderate with respect to the theoretical expectations. Indeed, the 2.5 nm MgO is below the asymptotic limit (large MgO thickness, where only *s*-like electrons of majority band tunnel). This argument is furthermore supported by a net signature of an IR state, located in the minority *d* band, on the tunnel transport characteristics. Moreover, one could alternatively consider the influence of a Fe-O layer at the interface Fe-MgO, related to the elaboration procedure [12]. Recent *ab initio* calculations [14] have shown that the interfacial Fe-O layer affects the propagation of the majority spin of Δ_1 symmetry in the MgO barrier, reducing the TMR ratio by reducing drastically the majority conductance.

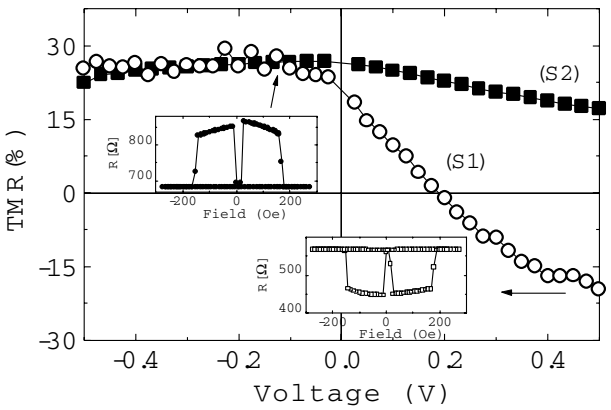

FIG. 2. TMR versus the voltage V curves measured in samples (S1) and (S2), respectively. Insets: Positive TMR versus magnetic field H [TMR(H)] curve measured at $V = -0.1$ V ($V+$ = top MTJ electrode); negative TMR(H) curve measured at $V = +0.5$ V ($V+$ = bottom MTJ electrode).

For positive biasing of the bottom electrode, the electrons, extracted from the top Fe(001) electrode by tunneling across the barrier, "scan" in energy the bottom "flat" Fe(001) electronic structure. Then, when the energy of the collected electrons "matches" the energy of the interface resonant state, a strong enhancement of the AP conductance with respect to the parallel one occurs, via the enhancement of the wave function matching at the interface. This is directly reflected by the sign reversal of the TMR (Fig. 2) and by the AP conductance which overcomes the parallel one above 0.2 eV [Fig. 3(a)]. However, when the interfacial state is not coupled to the bulk (S2), it will not provide a resonant-assisted enhancement of the AP conductance. Moreover, as illustrated by Fig. 3(b), the parallel conductance associated to the majority spin decreases with increasing the bias voltage. This counterintuitive effect simply reflects the electronic structure of Pd whose DOS vanishes abruptly above E_F [see Fig. 1(b)]. This influences directly the Bloch wave matching at the interfaces Pd/Fe/MgO, important for the propagation of electrons whose characteristic lengths (coherence/spin diffusion) overcome the thickness of the bottom Fe (tunneling electrons which see the Pd). Note that in a ferromagnetic material for the majority spin the diffusion length is larger than the one of minority. When the bias voltage is furthermore increased, the energy of hot electrons in the bottom Fe/Pd electrode increases, their characteristic lengths decrease. These electrons get rapidly thermalized to E_F, within the 2.5 nm Fe electrode. Consequently, the conductance becomes gradually insensitive to the Pd electronic structure. Let us now emphasize the influence of the top rough electrode. The disorder

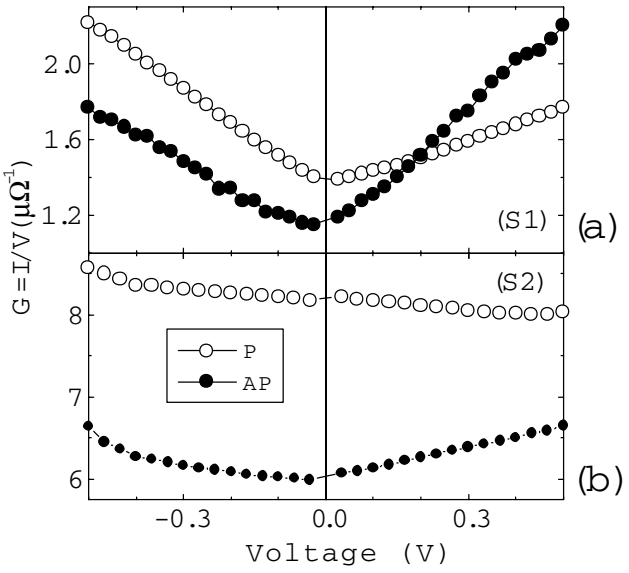

FIG. 3. Conductance versus voltage curves for samples (S1) (a) and (S2) (b) measured in parallel (○) and antiparallel (●) magnetic configurations of the MTJ electrodes, respectively.

breaks the symmetry of the system and mixes in terms of symmetry the propagating Bloch states in the leads [18]. This influences the tunneling of electrons injected towards the bottom flat one. It makes possible the injection and the tunneling of states which, due to their symmetry, would not be able to tunnel effectively through the barrier in perfect junctions. However, the electrons are "filtered" in symmetry by the barrier and the bottom flat Fe electrode (equivalent of a large band emitter and a narrow band filter). Therefore, the total conductivity of the junctions reflects the electronic properties of the bottom electrode and the interfacial band structure matching at the bottom Fe/MgO interface.

For negative voltage, when the electrons tunnel towards the rough top electrode positively biased, we observe a quasiconstant magnetoresistance versus V, up to an applied voltage of 0.5 V. Because of the interfacial roughness, one can easily assume that the interfacial DOS possesses no sharp feature and that no interfacial resonant state is present. It is worthwhile to remark here the enormous potential for applications of tunnel junctions where the TMR is "almost" constant with the bias voltage. The measured variation of the TMR with the bias voltage is very small ($V_{1/2} > 1.5$ V). It indicates that the mechanisms involved in the bias voltage variation of the TMR are not dominant in our MTJ. These mechanisms are (i) incoherent tunneling due to scattering at impurities or defects located in the barrier [10]; (ii) energy dependence of spin-polarized DOS, which affects the spin polarization [4]; and (iii) quenching of TMR by hot electrons or spin excitation of magnons [19]. In our monocristalline MTJ, the first mechanism is not dominant. Here, the quality of the insulator is rigorously controlled by the 2D epitaxial growth. As shown by Ding *et al.* [9], using indirect spin-polarized scanning tunneling microscopy measurements, in case of MTJs involving perfect thick vacuum barriers (asymptotic regime), the TMR as a function of the bias voltage is found to be constant. Concerning the second mechanism, one can assume that the energy dependence of spin-polarized DOS of a rough electrode, above the Fermi level, is small (no sharp features). This will translate an almost constant TMR versus V. This effect is furthermore enhanced by the symmetry dependent filtering of electrons by the bottom flat Fe "emitter" electrode and by the MgO barrier. These two filters favor the tunneling of dispersive s-like bands, whose DOS are smooth and extended [6]. Moreover, when the junction is biased, one cannot neglect the contribution to the tunneling of the electrons from the negatively biased electrode located below the Fermi level within an energy range $[E_F - eV, E_F]$. They will tunnel into the positively biased electrode within a $[E_F, E_F + eV]$ unoccupied band. This would implicate an extremely complex analysis of the tunneling in a nonequilibrium biased MTJ stack for electrons coming beyond the Fermi level. Lastly, one can assign the slight variation of the TMR with V in our junctions to the third mechanism, implicating interfacial magnons.

In summary, by using spin dependent tunnel transport characteristics of model monocrystalline Fe/MgO/Fe-type MTJ systems, we pointed out the influence of the interfacial states on the spin-polarized tunneling. In our samples the electronic structure of the Fe/MgO interface is controlled via the topological quality of the Fe layers. We show that, in order to contribute to the total conductance, the interfacial state has to be coupled to the bulk. Last, one should remark that in high-quality epitaxial junctions the spin-polarized current voltage characteristics can be controlled via the engineering of the electronic structure of the layers, a fact extremely important for potential applications of the MTJs.

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