Interfacial Density of States in Magnetic Tunnel Junctions

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Large zero-bias resistance anomalies as well as a collapse of magnetoresistance were observed in $Co/Al_2O_3/Co$ magnetic tunnel junctions with thin Cr interfacial layers. The tunnel magnetoresistance decays exponentially with nominal Cr interlayer thickness with a length scale of ~1 Å more than twice as fast as for Cu interlayers. The strong suppression of magnetoresistance, as well as the zero-bias anomalies, can be understood by considering a strong spin-dependent modification of the density of states at Co/Cr interfaces. The role of the interfacial density of states is shown by the use of specially engineered structures. Similar effects are predicted and observed in junctions with Ru interfacial layers.

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Since the recent discovery of large magnetoresistance in magnetic tunnel junctions [1], there has been a renewed technological and fundamental interest in the tunneling phenomenon. In general, tunneling is considered to be an extremely interface sensitive technique [2–5], with the transport properties determined primarily by the density of states at the electrode-barrier interface [6,7]. In view of this apparent interface sensitivity, systematically altering or engineering the electrode-barrier interfaces in tunnel structures, e.g., by the use of interfacial layers, is a natural way to gain understanding about these devices. Surprisingly, only a few experiments [4,5,8,9] of this nature have been reported in relation to magnetic tunnel junctions. These experiments have primarily utilized interfacial layers inserted at the ferromagnetic electrode-barrier interface ("dusting" layers) in an attempt to clarify the role of the interfacial density of states. However, some of these experiments have been difficult to interpret due to growth-related artifacts [9], though in general it is found that the tunneling magnetoresistance (TMR) decays rapidly, on a monolayer scale, as a function of interlayer thickness.

Theoretically, several models have been advanced [10–14] for magnetic junctions with nonmagnetic interfacial layers. In contrast to the aforementioned experimental data, these models generally predict that sizable TMR is maintained for relatively large interfacial layer thicknesses, and in some cases that the TMR oscillates as a function of thickness. Thus, it seems that these models do not capture the experimentally observed interface sensitivity of tunneling structures.

In order to clearly attribute spin-dependent tunneling transport properties to an interfacial density of states, a system in which the density of states may be modified in a well-known way is needed. The electronic structure of ferromagnetic-nonmagnetic (FM-NM) interfaces has received special attention in relation to the giant magnetoresistance effect in metallic multilayers. In this case, the degree and spin asymmetry of interfacial scattering can be explained by considering the band matching between FM majority/minority bands and the NM bands [15–17] at interfaces or within intermixed regions. Among Co-3d metal interfaces, this asymmetry is maximal for Cr [16] (as is also the case for 3d impurities in Co [18,19]), while among Co-4d metal interfaces maximal asymmetry occurs for Ru [16,18,19]. Since the band mismatch is largest in these cases, the resulting interfacial density of states modification is also the largest. In this light, Co-based magnetic tunnel junctions with Cr and Ru interfacial layers seem to be ideal candidates for investigating interface sensitivity and the role of interfacial electronic structure.

In this Letter, we will present evidence on the genuine interface sensitivity of tunneling by the use of specially engineered tunneling structures utilizing *multiple interfacial layers, designed to strongly modify the interfacial density of states*. We will show that, by analyzing conductance-voltage characteristics in these structures, the TMR decrease may be correlated with the interfacial electronic structure. In striking contrast to earlier reported results for Cu interlayers [8,20], for Cr interlayers the TMR decays more than twice as fast, near vanishing by ~1 monolayer (ML) Cr. As we will argue, this extremely rapid TMR collapse can be qualitatively explained in terms of a strongly modified density of states at the (interdiffused) Co-Cr interface, as in magnetic multilayers [17] and dilute Co-based alloys [18,19]. In addition to the strong TMR decrease, we report strong zero-bias anomalies in junctions with Cr, with a strong suppression of the conductance about $V = 0$. Utilizing $Co/M_1/M_2/Al_2O_3/Co$ ($M_{1,2}$ = Co, Cu, Cr) junctions, we will demonstrate that the Co-Cr interface is specifically responsible for the zero-bias anomalies and clearly confirm the extreme interface sensitivity of tunneling. We argue that both the conductance results, as well as the TMR results, can be explained in terms of the same strong (spin-dependent) density of states modification at the Cr-Co interface, in analogy with mechanisms for zero-bias anomalies in *nonmagnetic* tunnel junctions with magnetic impurities [7,21]. Finally, we will validate our conjectures by using another system with a large interfacial density of states modification, viz., Co-Ru.

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Ferromagnetic tunnel junctions were prepared by UHV dc/rf magnetron sputtering (base pressure $<5 \times 10^{-10}$ mbar) through metal contact masks onto plasma oxidized Si(100) substrates. The details of this fabrication process have been described elsewhere [8,20]. Dusting layers were inserted at the *bottom* Co/Al_2O_3 interface [8] to avoid spurious effects due to clusterlike growth. *In situ* x-ray photoelectron spectroscopy and optical techniques were used to confirm that there was no electrode (Co) or dusting layer (Co, Cu, Cr, Ru) oxidation, with a minimal amount of remaining metallic Al [8,22]. Junction resistances and conductances $[dI/dV \equiv G(V)]$ or dynamic resistances $[dV/dI = G^{-1}(V)]$ were measured using standard ac lock-in techniques, with the ac excitation kept well below $k_B T$ to avoid modulation broadening. TMR ($\Delta R/R_p$ or $\Delta G/G_a$) was measured using both dc and ac lock-in techniques.

Figure 1 shows the normalized TMR at 10 K as a function of nominal Cr dusting layer thickness ($Co/Cr\ d_{Cr}/Al_2O_3/Co$). In contrast to previous results with Cu dusting layers, where an exponential decrease with a length scale of $\xi \sim 2.6$ Å was found, the magnetoresistance decay for Cr dusted junctions is considerably faster, giving a length scale of nominally 1.25 Å (1.0 Å) at 10 K (295 K). With the addition of only 3 Å Cr (approximately 1.5 ML), the reduced TMR is only 10% of that for a control junction. However, by subsequently covering the Cr with 6.3 or 10 Å Co ($Co/Cr\ d_{Cr}/Co\ d_{Co}/Al_2O_3/Co$), the TMR is nearly completely restored, saturating at approximately 75% of that for a control junction. This clearly demonstrates not only the dramatic effect of Cr interlayers on tunnel spin polarization, but also the truly interfacial nature of the spin polarization reduction, illustrating that only a few monolayers adjacent to the tunnel barrier are important for tunneling [2].

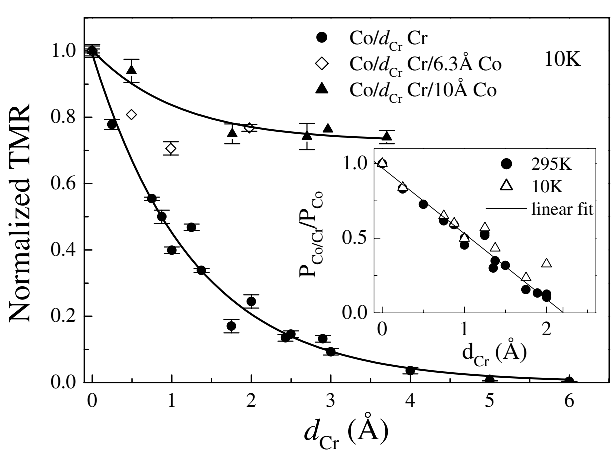

FIG. 1. Normalized TMR as a function of Cr interlayer thickness for junctions dusted with only Cr, and Cr with Co (6.3 Å, 10.0 Å), showing the near complete restoration of the original TMR. Lines are a guide to the eye. Inset: Co/Cr spin polarization deduced from the Julliere model (see text) as a function of Cr interlayer thickness for 10 K (triangles) and 295 K (circles); the line is a linear fit for 295 K.

Using the relation introduced by Julliere [23] as a simple first-order approximation [3], we may relate the measured TMR values to an effective tunneling spin polarization: $\mathrm{TMR} = 2P_1P_2/(1 - P_1P_2)$ where P_1 and P_2 are the effective spin polarizations of the first and second tunneling electrodes. As shown by the inset of Fig. 1, for submonolayer amounts of Cr, the polarization decreases rapidly to near zero values, and if extrapolated, corresponds to a complete destruction of the spin polarization at $\sim$1 ML Cr.

From studies on Co-Cr multilayers [17] and alloys [18,19], it is known that a mismatch between majority spin d levels of Co and Cr prevents hybridization of these bands. The resonant scattering of majority spin s-p electrons with Cr d states results in the majority spin density of states becoming highly localized at Cr sites (i.e., the formation of a virtual bound state leads to a high majority spin density of states near the Fermi level on Cr sites). The s-p density of states is then suppressed more strongly for majority spins than minority spins. Since tunneling is particularly sensitive to s-p electrons [2,3], and samples only the *interfacial* density of states [2,6], we may attribute the strong spin polarization reduction to the spin-dependently modified density of states at the Co-Cr interface. This may also be viewed in terms of the magnetism of Co-Cr alloys. We point out that the Co-Cr interfaces are expected to be significantly interdiffused [24] (few ML's), and for the extremely thin Cr layers used here, we may consider the dusting layer as either a Co-Cr alloy or an intermixed Co-Cr interface (despite this fact, we will continue to refer to the dusting layers in terms of nominal Cr thicknesses). For bulk Co-Cr alloys, the magnetic moment is strongly reduced, with the alloy becoming nonmagnetic at $\approx$25% Cr [25,26], a composition which may easily be reached at Co-Cr interfaces in the range of thicknesses used.

In addition to the rapid TMR decrease, Cr dusted junctions also showed unusual conductance-voltage and conductance-temperature behavior. Figure 2(a) shows conductance vs voltage for a junction with 6.1 Å Cr measured at various temperatures, as well as a control junction at 10 K. Strong zero-bias anomalies are present compared to a control junction, with the conductance vs voltage changing by as much as a factor of 2 in only $\sim$100 mV. The narrow energy width of the anomaly is seen clearly, where the zero-bias conductance changes much more rapidly than conductance at higher biases. Figure 2(b) shows conductance (dI/dV) vs temperature data for a control junction and a junction with 6.1 Å Cr (measured at $V \approx 0$). Measurements on many Co-Co control junctions routinely show 10%–15% change in resistance from 10–300 K, in good agreement with reported work [27], which has been explained by a reduction of the surface magnetization with temperature [27]. For junctions with Cr measured at *low voltages*, an extremely strong temperature dependence is exhibited relative to control junctions, and the temperature dependence is in general stronger for thicker Cr interlayers. The zero-bias

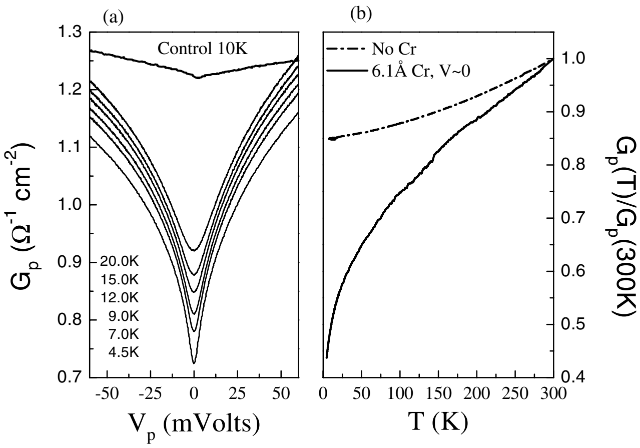

FIG. 2. (a) Conductance vs voltage at various temperatures for a junction with 6.1 Å Cr as well as a control junction at 10 K. The control junction curve has been vertically shifted for clarity. (b) Conductance vs temperature (normalized to 300 K) for junctions with no Cr and 6.1 Å Cr.

conductance minima were present even at 300 K, with a width of approximately k_BT, suggesting that the temperature dependence of the zero-bias conductance results only from thermal smearing of a near-singular density of states. The temperature and voltage dependence are roughly logarithmic for low bias and temperature, though we note that the *resistance* may be just as convincingly shown to be logarithmic, as found by previous authors [28]. We will return to the origin of the zero-bias anomalies, as well as their possible relation to the rapid TMR decrease, later on.

Multiple dusting layers can be used to experimentally establish that the Co/Cr *interface* is specifically responsible for these zero-bias anomalies. Figure 3(a) shows G_p vs applied bias for a control junction, a junction dusted with 1.8 Å Cr, and a junction dusted with 1.0 Å Cr + 6.3 Å Co. Compared to a junction with Cr at the interface, when the Cr layer is positioned a few ML's (6.3 Å) away from the interface the "anomalous" effects have nearly disappeared. As pointed out earlier, this is also accompanied by an almost full restoration of the tunneling spin polarization. In addition, Cu interlayers were used to show that Cr *in contact with* Co is responsible for the anomalous behavior. Shown in Fig. 3(b) are G_p vs voltage characteristics for junctions with 1.8 Å Cr, 3.0 Å Cu, 1.8 Å Cr + 3.0 Å Cu, and 3.0 Å Cu + 1.8 Å Cr dusting layers. For Cu dusting, no anomalies are seen [20], while for Cr dusting extremely strong anomalies are observed. However, for dusting layers of 3.0 Å Cu + 1.8 Å Cr, the anomaly strength is reduced by roughly a factor of 10, despite the fact that the Cu thickness is only ≈1.5 ML. It is clearly seen that when Cr is at the interface but backed with Cu rather than Co, the anomaly strength is much reduced, indicative of the *magnetic nature* of the anomalies. Finally, to show that the Co-Cr interface is responsible for the effects, rather than the Cr-Al_2O_3 interface (or Cr within the Al_2O_3), a Co electrode was dusted with 1.8 Å Cr + 3.1 Å Cu [Fig. 3(b)]. In this case, the anomaly is clearly still present, though approximately a factor of 5 weaker than for 1.8 Å Cr alone. The anomaly is approximately a factor of 2 stronger for the Co/Cr/Cu combination compared to the Co/Cu/Cr combination, further indicating that the Co/Cr interface plays the dominant role.

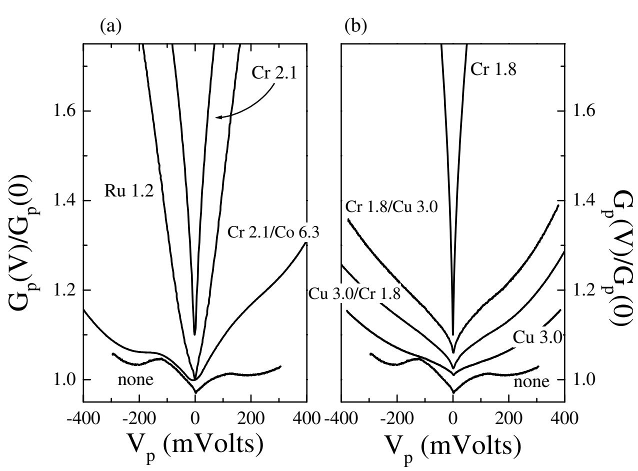

FIG. 3. (a) Normalized parallel conductance for junctions with no dusting layer, and dusting layers of (2.1 Å Cr + 6.3 Å Co), 2.1 Å Cr, and 1.2 Å Ru. (b) As in (a) for no dusting layer, 3.0 Å Cu, (3.0 Å Cu + 1.8 Å Cr), (1.8 Å Cr + 3.0 Å Cu), and 1.8 Å Cr. Multiple dusting layers clearly demonstrate the role of the Co-Cr interface. Some curves have been vertically shifted for clarity.

Returning once again to the underlying physical mechanisms, large zero-bias anomalies have been extensively studied [21] specifically in nonmagnetic junctions where magnetic impurities or impurity layers were placed within one of the electrodes or within the insulating barrier. For magnetic impurities within a nonmagnetic electrode, the anomalies were explained by considering the modification of the interfacial density of states by the impurities [7,29]. Mezei and Zawadowski [7] found theoretically that the tunnel conductance is proportional to the local density of states at the electrode-barrier interface, which is in turn inversely proportional to the *s-d* scattering amplitude. Essentially, the logarithmic zero-bias anomalies measure the energy dependence of the Kondo scattering amplitude. Although their work may not be directly applicable to the present case (which deals with magnetic junctions), we may understand the present experiments based on these ideas. We feel that the strongly depressed density of states at Co-Cr interfaces (particularly for majority spins) induced by resonant scattering, as discussed earlier, essentially fulfills the requirements of Mezei and Zawadowski for observing strong zero-bias anomalies. If we further conjecture that Cr moments in Co/Cr are spin fluctuating [18], Kondo-like behavior could be anticipated, and the model of Mezei and Zawadowski would be more applicable. In other words, we probe the energy-dependent scattering of conduction electrons by fluctuating Cr moments. The strong similarities between their model and our results for Cr on Co clearly point to an explanation related to a strongly modified local density of states. Parenthetically, we do *not* suggest that the zero-bias anomaly reflects *directly* the Co/Cr density of states, but, rather, energy-dependent electron-electron scattering at the Co/Cr interface.

In order to validate our conjectures about zero-bias anomalies, we have also prepared junctions with Ru dusting layers. For 4*d*-metal interfaces with Co, as well as for impurities in Co, it is Ru which shows the maximal scattering cross section as well as the largest spin asymmetry, and hence the strongest modification of the interfacial density of states [16,18,19]. Further, NMR studies [30] on Co-Ru multilayers indicate strong interdiffusion ($\sim$2 ML per interface), and a description in terms of Ru impurities in Co is reasonable. If an explanation based on a strongly altered interfacial density of states and spin fluctuations is correct, it is expected that junctions with Ru interlayers should behave similarly to those with Cr interlayers. Figure 3(a) shows $G_p(V)$ for a control junction, a junction with 2.1 Å Cr, and a junction with 1.2 Å Ru. As with Cr, junctions dusted with Ru indeed also exhibit large zero-bias anomalies, with the conductance changing by more than a factor of 2 within 300 mV, supporting our explanation. Further, the TMR decrease observed for Ru interlayers is analogous to that for Cr interlayers, viz., $\xi_{\mathrm{Ru}} \sim 1$ Å, with a near zero effective spin polarization for Ru thicknesses greater than $\sim$1 ML. We emphasize here again that Cu interlayers show no zero-bias anomalies [20], and exhibit a decay length more than a factor of 2 longer than for either Cr or Ru interlayers [8]. For Cu on Co, the resonant scattering condition is not fulfilled (i.e., the virtual bound state is far from the Fermi level), and thus the strong suppression of the local density of states is not expected as for Cr or Ru on Co [16,17]. One can also view this in terms of the more drastic effect of Cr and Ru on the interface magnetism compared to Cu. Further, for Co-Cu, a relatively sharp interface was observed [8], and thus a description in terms of Cu impurities in Co is less valid.

In conclusion, we have experimentally established the dramatic role of the interfacial density of states in (magnetic) tunnel junctions. We have also, utilizing TMR and conductance-voltage characteristics, given experimental indications for the underlying mechanisms. A more complete theoretical picture is clearly needed—the model of Mezei and Zawadowski [7] needs to be extended to the case of magnetic electrodes, or alternatively, the model of Itoh *et al.* [15,16] needs to be extended to tunneling structures. Once the role of interfacial density of states effects is more completely understood, magnetic tunneling structures may perhaps be engineered for improved magnetoresistive properties.

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