Spin Tunneling in Junctions with Disordered Ferromagnets

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We provide compelling evidence to establish that, contrary to one’s elementary guess, the tunneling spin polarization (TSP) of amorphous CoFeB is larger than that of fcc CoFeB. First-principles atomic and electronic structure calculations reveal striking agreement between the measured TSP and the predicted s-electron spin polarization. Given the disordered structure of the ternary alloy, not only do these results strongly endorse our communal understanding of tunneling through AlO3, but they also portray the key concepts that demand primary consideration in such complex systems.

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Right from its inception, experimental and theoretical endeavors in electron tunneling have been dedicated to the understanding of the role of the electrode and barrier electronic structure. For ferromagnetic films, one aspect of their electronic structure—the tunneling spin polarization (TSP)—was measured with superconducting tunneling spectroscopy (STS) by Meservey and Tedrow [1]. Although some preliminary effort was undertaken to study the role of the band structure of ferromagnetic films in tunneling [2], no definitive observations were made till the advent of tunnel magnetoresistance (TMR) in magnetic tunnel junctions (MTJs). Then, Yuasa et al. [3] and LeClair et al. [4] experimentally demonstrated the influence of epitaxial Fe and textured Co films on TMR and tunneling conductance, respectively. Regarding the nature of the electronic wave functions that govern the tunneling probability through AlO3, the dominance of the spherically symmetric s-like electrons has been experimentally demonstrated [5,6]. Recently, spintronics has witnessed a rapid rise in the importance of amorphous ferromagnets like CoFeB. They have contributed to huge TMR in AlO3 [7] and MgO [8] based MTJs. They have also been used to observe the novel spin-torque diode effect [9] and facilitated record-low switching currents in spin-torque based MTJs [10]. Although their emerging importance in spintronics is unquestionable, neither has there been a theoretical and experimental analysis of their atomic and electronic structure, nor has the impact of these properties on their TSP been investigated.

In this Letter, we explore the correlation between ferromagnet morphology, its electronic structure, and their combined impact on TSP. One unique aspect—crystallization of amorphous CoFeB with a single high temperature anneal (≥250 °C [11])—is exploited to study the structural, magnetic, and TSP related properties of amorphous and crystalline CoFeB in the same sample. Indeed, such control on morphology is not accessible in elemental magnetic films. The high temperature anneal stipulates a crucial requirement for our junctions; viz., the barrier properties should not change after annealing to ensure comparison between the TSP of as-deposited and annealed CoFeB. Contrary to alternative barriers like MgO, AlO3 barriers are known to exhibit no TSP related changes after anneals up to Tanneal = 500 °C [12,13]. When the structure of Co72Fe38B8 is intentionally transformed from amorphous to highly textured fcc, we notice that a correlated alteration of the CoFeB electronic structure is induced. Contrary to one’s primary intuition, this alteration of the electronic structure manifests in an intrinsically larger TSP for amorphous CoFeB as compared to that of highly textured fcc CoFeB. First-principles atomic structure calculations of amorphous CoFeB are found to be consistent with extended x-ray absorption fine structure (EXAFS) measurements. Remarkably, electronic structure calculations based on this atomic structure exhibit a conspicuous agreement between the spin polarization (SP) of the s-electron density of states (DOS) and the experimentally measured TSP, both for amorphous and crystalline CoFeB. The calculations also reveal that the B sp states get highly spin polarized and make a significant contribution to the alloy SP. We would like to emphasize that such a quantitative agreement between theory and experiment for a complex amorphous-crystalline ternary alloy has not been reported before. Moreover, given the recent development in CoFeB based spintronic devices, first-principles atomic and electronic structure calculations, especially those corroborating spin-polarized tunneling experiments, have not been reported yet. Furthermore, these results endorse several earlier concepts, for example, the high sensitivity of the tunnel conductance to the ferromagnet-barrier interface [14], and the dominance of s electrons in tunneling through AlO3 [5,6].

The inset in Fig. 1(a) shows a representative TSP measurement for an as-deposited 120 Å CoFeB film using STS [1]. Regardless of the CoFeB thickness (d), for as-deposited samples, we consistently measure a TSP above

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A clue to the probable reason behind this change in the TSP of thin CoFeB films can be found in x-ray diffraction (XRD) measurements on films of corresponding thickness. In Fig. 1(b), the grain size perpendicular to the film plane, calculated using the Paul Scherrer formula, and normalized to the film thickness, is plotted as a function of $T_a$. This plot indicates that, in progressively thinner films, the grain sizes become comparable to the film thickness after the anneal. For $T_a = 450 \degree C$ and $d = 120 \AA$, the average grain size is almost equal to the film thickness, suggesting the presence of crystalline CoFeB at the interface with the AlO$_x$ barrier. This hypothesis is substantiated by high resolution transmission electron micrographs (HRTEM). Figure 1(c) shows a junction with a 700 $\AA$ CoFeB layer, while Fig. 1(d) corresponds to a 60 $\AA$ CoFeB layer, both annealed at 450 $\degree C$. For the 700 $\AA$ film, a close inspection of the barrier-ferromagnet interface region shows hardly any crystalline CoFeB at the interface, though we observe CoFeB crystallites in the bulk of the film (not shown). In sharp contrast, we observe almost comprehensive crystallization of CoFeB in the case of the 60 $\AA$ film, especially at the barrier-ferromagnet interface. Together, the XRD and HRTEM data strongly advocate that thicker films ($d \geq 500 \AA$) do not crystallize completely after the anneal, especially at the interface with amorphous AlO$_x$, and consequently show a TSP similar to that of as-deposited amorphous CoFeB. On the contrary, thinner films crystallize virtually completely, and the TSP of crystalline CoFeB at its interface with AlO$_x$ manifests its intrinsic value. Note that the interface sensitivity of the TSP [14] is implicitly demonstrated within this inference. Furthermore, consistent with the observations of Takeuchi et al. [15], in crystalline films, the out-of-plane grain size is limited by the film thickness, while the in-plane grain size (150–200 $\AA$) is similar to that observed in thicker films. As anticipated for such a Co rich composition, high angle XRD also confirms that CoFeB crystallizes in a highly (111) textured fcc structure.

Having established that the lowering of the CoFeB TSP is closely related to its crystallization, we embark on first-principles calculations using density functional theory within the generalized gradient approximation [16]. The self-consistent electronic structure and interatomic forces are calculated with the projector augmented wave method [17] using the Vienna ab initio molecular dynamics package (VASP) [18]. For reliable determination of the amorphous structure, the ensemble is heated above its melting point and equilibrated in the liquid state for time periods long enough to allow diffusion beyond one lattice spacing, and then rapidly quenched to form the amorphous state. Structural and electronic properties of two 108 atom ensembles are compared to three 54 atom ensembles for further verification and statistics. It is noteworthy that ensembles without B atoms do not quench in an amorphous structure, indicating the key role played by $\sim 7$ at. % B in rendering CoFeB amorphous. In the fcc case, the atoms are...
The oscillations seen in Fig. 2(e) are characteristic of the alloy [19] on Co$_{100-x}$Fe$_x$, which show that the Fe magnetic moment increases with increasing $x$-band width is observed to be slightly lower in the amorphous case as compared to the fcc case. This follows from the increase in the average Co-Co and Fe-Fe distance in the amorphous case [Figs. 2(c) and 2(d)] where the first coordination shell loses ~1 atom and the second coordination shell around 3.5 Å is almost completely wiped out in comparison to the fcc case.

Considering the amorphous nature of the barrier, one might argue that $k$-conservation is highly unlikely in tunneling through AlO$_x$. In the first instance, if one neglects any issue related to the barrier or interface electronic structure, the SP of $s$-like electrons, which have been experimentally shown [5,6] to dominate tunneling through AlO$_x$, is the only quantity that needs consideration. Table I shows the calculated average $s$-electron SP at the Fermi level ($E_F$) for Co, Fe, and B in the amorphous and fcc case. Assuming that the concentration at the interface is similar to that in the bulk, we obtain the alloy SP by weighting these individual SPs with their concentrations [1]. The last columns of Table I compare the measured TSP to the calculated alloy SP. For both the amorphous and fcc case, the calculated SPs of 50% ± 0.2% and 41% ± 0.5% are in surprisingly good agreement with the measured TSPs of 53% ± 0.5% and 44% ± 0.5%, respectively. Most strikingly, the difference of ~9% between the two measured TSP values is directly reflected in the calculations as well, indicating that this difference may arise from the disparity in the band structure of bulk amorphous and fcc CoFeB. It is noteworthy that the values of the element-specific and the alloy SPs are remarkably similar from one unit cell to another for the 5 amorphous and 2 fcc unit cells studied. The errors in Table I are deduced from the variations in the element-specific SPs under a coarse and a fine sampling of $k$ space.

Interface bonding effects have been calculated to have pronounced effects on the TSP [20]. However, given the amorphous nature of AlO$_x$, these are rather difficult to predict, and in reality, they are an average over the con-
Co (and Fe) are pushed towards higher energy for both amorphous case as compared to the fcc case. Consequently, alloy might be responsible for this [Figs. 2(c) and 2(d)]. The specific EF shift of the antibonding states toward higher energy, since alloy as given in Table I. If one compares the element-CoFeB, which confirms the higher SP of the amorphous structure of both the electrode and the barrier, one might wonder if a better quantitative agreement can be achieved by going into further complexity.

Figure 3(b) shows the total s-DOS of amorphous and fcc CoFeB, which confirms the higher SP of the amorphous alloy as given in Table I. If one compares the element-specific s-DOS for amorphous Co (and Fe—not shown) to fcc Co (and Fe) in Fig. 3(c), the antibonding s states of fcc Co (and Fe) are pushed towards higher energy for both spin channels. Increased s-d hybridization due to an increase in the first and second shell coordination of the fcc alloy might be responsible for this [Figs. 2(c) and 2(d)]. Interestingly, the decrease in the s-electron SP of the fcc alloy might be seen to primarily ensue from this spectral shift of the antibonding states toward higher energy, since $E_F$ lies on the slope of the increasing majority s-DOS, while lying in the deep minimum of the minority s-DOS. One notices from Fig. 3(b) that the minority DOS also shows subtle changes, which provide a secondary contribution to the change in the s-electron SP. The impact of s-d hybridization can also be seen in the B s-DOS shown in Fig. 3(d). In our calculations we note that (1) the B sp states are highly spin polarized (s-SP > 50%; p-SP > 25%) as noted before [22], and (2) the B sites attain a small negative magnetic moment ($\sim 0.1 \mu_B$) consistent with earlier work [23]. This high SP is a direct consequence of the hybridization of the B sp states with the Co/Fe d states [24]. From the pRDFs of Co-B [see inset in Fig. 3(d)] and Fe-B (not shown), one notes that the peak in the first coordination shell around 2.1 Å is larger in the amorphous case as compared to the fcc case. Consequently, for amorphous CoFeB, this leads to increased s-p-d hybridization and the antibonding s states of B are shifted to higher energy as seen in Fig. 3(d). Here, however, the SP increases compared to the fcc case due to the lower minority s-DOS at $E_F$. Moreover, we stress that the SP of B s states has a direct impact on the TSP. The fifth column in Table I shows the calculated average SP of the alloy when the B atoms are considered unpolarized. The obvious disagreement with the measured TSP is an indication of the importance of highly spin-polarized B atoms at the interface.

In summary, we show that in AlO$_x$ based junctions, the TSP of amorphous CoFeB is larger than that of fcc CoFeB. Calculations of the atomic and electronic structure of amorphous and fcc CoFeB yield s-electron SP values in remarkable agreement with experiment. These observations demonstrate that the electronic structure of the electrode has a marked impact on tunneling, and the SP of such a complex ternary amorphous-crystalline alloy can be genuinely calculated.

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